Construction of Supported Organometallics Using Cycloplatinated Arylamine Ligands

Michel D. Meijer,[†] Arjan W. Kleij,[†] B. Scott Williams,[†] Dianne Ellis,[‡] Martin Lutz,[‡] Anthony L. Spek,[‡,§] Gerard P. M. van Klink,[†] and Gerard van Koten*,[†]

Department of Metal-Mediated Synthesis, Debye Institute, Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands, and Department of Crystal and Structural Chemistry, Bijvoet Center for Biomolecular Research, Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands

Received June 11, 2001

The preparation of *ortho*-chelating aminoaryl ligands ($[C_6H_3(CH_2NMe_2)$-2-R-4$]^-$, abbreviated as C,N) containing a pendant hydroxymethyl group is described. These ligands have been cycloplatinated with *cis*-$PtCl_2(DMSO)_2$, yielding the corresponding C,N-platinum(II) complexes. The pendant hydroxymethyl substituent is a versatile group for attachment of the organometallic moiety to macromolecules, which has been demonstrated by attaching the C,N-platinum complexes to a dendritic wedge and to C_{60}.

Introduction

One of the most rapidly developing fields in organometallic chemistry is the construction of supramolecular structures[1] and organometallic assemblies.[2] In some cases, the macromolecular structures contain (metal) sites or functional groups that can lead to new materials, applicable in host−guest chemistry[3] and catalysis[4] or as sensors.[5] In the construction of these materials, organometallic moieties have been introduced via a ligand modification/immobilization and subsequent metalation step, which is not always the optimal procedure. For example, we have encountered unexpected inter- and intramolecular complexation behavior of C,N-derivatized carbosilane dendrimers (C,N = C,N-chelating $[C_6H_3(CH_2NMe_2)$-2-R-4$]^-$) during metalation steps, resulting in the formation of multimetallic aggregates.[6]

An approach to circumvent these interactions involves the attachment of a complete organometallic moiety to a macromolecular structure or to a support. This has been successfully demonstrated with supports such as silica surfaces,[7] (hyperbranched) polymers,[8] dendrimers,[9] and more recently, for the functionalization of the periphery of dendrimers with NCN-palladium(II) and -platinum(II) complexes (NCN = $[C_6H_2(CH_2NMe_2)_2$-2,6-R-4$]^-$), yielding macromolecular catalysts and SO_2–sensing dendritic macromolecules, respectively.[5,10] To develop this approach for the C,N-ligand, we have studied the synthesis and structural characterization of a series of cycloplatinated C,N-derived ligands containing a pendant hydroxymethyl group (*para* to the CH_2NMe_2 substituent). This group serves as a suitable linker for attachment of the organometallic fragment to the macromolecular framework. In this fashion, C,N-platinum(II) complexes have been anchored to a Fréchet-G1 dendron and to C_{60}.

Results and Discussion

Synthesis and Characterization of Cycloplatinated C,N-Complexes. Synthetic protocols were developed for cycloplatinated C,N-complexes containing a hydroxymethyl group, which can be used as a linker to attach the organoplatinum fragment to a macromolecular structure. 4-[(Dimethylamino)methyl)]benzaldehyde was reacted with $LiAlH_4$, affording benzyl alcohol **1** (Scheme 1). Direct cycloplatination of **1** with an equimolar amount of *cis*-$PtCl_2(DMSO)_2$ in the presence of NaOAc yielded the platinum DMSO derivative **2**, which was converted into the corresponding triphenylphosphine derivative **3** via ligand exchange.

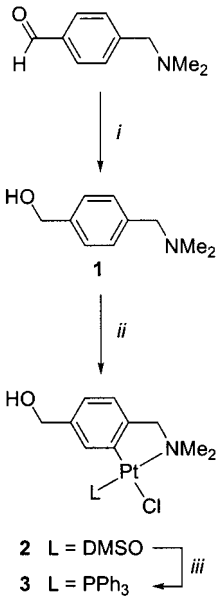
To double the number of organometallic units per hydroxyl linking group, the bis(H-C,N)-ligand **4** has also been prepared (Scheme 2). Treatment of 4-[(dimethylamino)methyl)]benzaldehyde with an equimolar amount

* To whom correspondence should be addressed. E-mail: g.vankoten@chem.uu.nl. Fax: +(31) 30 2523615.
† Debye Institute.
‡ Bijvoet Center for Biomolecular Research.
§ Address correspondence pertaining to crystallographic studies to this author. E-mail: a.l.spek@chem.uu.nl.

(1) Lehn, J.-M. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1304.
(2) (a) Stang, P. J.; Olenyuk, B. *Acc. Chem. Res.* **1997**, *30*, 502. (b) Leininger, S.; Olenyuk, B.; Stang, P. J. *Chem. Rev.* **2000**, *100*, 853.
(3) Vögtle, F. *Comprehensive Supramolecular Chemistry*; Pergamon/Elsevier Press: New York, 1997; Vol. 2.
(4) (a) Sanders, J. K. M. *Chem. Eur. J.* **1998**, *4*, 1378. (b) Kirby, A. J. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 707.
(5) (a) Albrecht, M.; Gossage, R. A.; Spek, A. L.; van Koten, G. *Chem Commun.* **1998**, 1003. (b) Albrecht, M.; van Koten G. *Adv. Mater.* **1999**, *11*, 171. (c) Albrecht, M.; Lutz, M.; Spek, A. L.; van Koten, G. *Nature* **2000**, *406*, 970.
(6) (a) Kleij, A. W.; Kleijn, H.; Jastrzebski, J. T. B. H.; Smeets, W. J. J.; Spek, A. L.; van Koten, G. *Organometallics* **1999**, *18*, 268. (b) Kleij, A. W.; Klein Gebbink, R. J. M.; van den Nieuwenhuijzen, P. A. J.; Kooiman, H.; Lutz, M.; Spek, A. L.; van Koten, G. *Organometallics* **2001**, *20*, 634.
(7) (a) Price, P. M.; Clark, J. H.; Macquarrie, D. J. *J. Chem. Soc., Dalton Trans.* **2000**, 101. (b) Macquarrie, D. J.; Fairfield, S. E. *J. Mater. Chem.* **1997**, *7*, 2201. (c) van de Kuil, L. A.; Grove, D. M.; Zwikker, J. W.; Jenneskens, L. W.; Drenth, W.; van Koten, G. *Chem. Mater.* **1996**, *6*, 1675.
(8) Schlenk, C.; Kleij, A. W.; Frey, H.; van Koten, G. *Angew. Chem., Int. Ed.* **2000**, *39*, 3445.
(9) For reviews on this subject, see: (a) van Koten, G.; Jastrzebski, J. T. B. H. *J. Mol. Catal. A* **1999**, *146*, 317. (b) Majoral, J. P.; Caminade, A.-M. *Chem. Rev.* **1999**, *99*, 845. (c) Newkome, G. R.; He, E.; Moorefield, C. N. *Chem. Rev.* **1999**, *99*, 1698. (d) Bosman, A. W.; Janssen, H. M.; Meijer, E. W. *Chem. Rev.* **1999**, *99*, 1665.
(10) Dijkstra, H. P.; Albrecht, M.; Ronde, N.; van Klink, G. P. M.; Vogt, D.; van Koten, G., to be published.

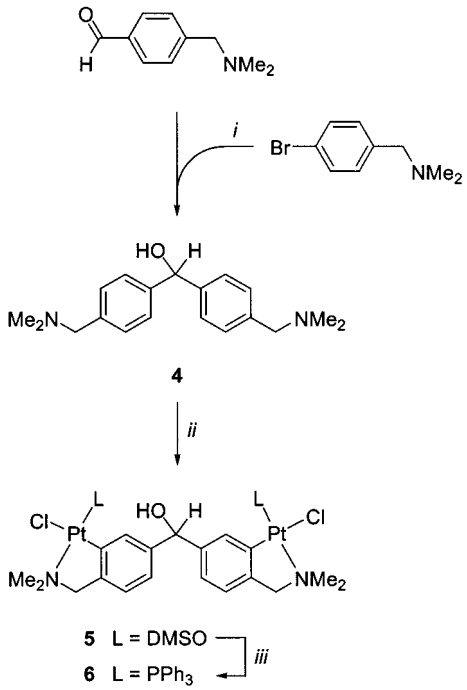
10.1021/om010500g CCC: $22.00
Publication on Web 12/19/2001

Scheme 1. Synthesis of 3[a]



[a] Reagents and Conditions: (i) $LiAlH_4$, Et_2O, 0 °C; (ii) *cis*-$PtCl_2(DMSO)_2$, NaOAc, MeOH, 65 °C; (iii) PPh_3, CH_2Cl_2.

Scheme 2. Synthesis of 6[a]



[a] Reagents and Conditions: (i) 2 equiv of *t*-BuLi, Et_2O, −78 °C to rt; (ii) 2 equiv of *cis*-$PtCl_2(DMSO)_2$, 2 equiv of NaOAc, MeOH, 65 °C; (iii) 2 PPh_3, CH_2Cl_2.

of the lithium reagent [Li{$C_6H_4(CH_2NMe_2)$-4}] in diethyl ether yielded the bis(H-C,N)-functionalized derivative **4**. The introduction of a platinum center in each of the two C,N-sites was achieved using the same methodology as described for **2**, producing the bisplatinum compound **5** as a white solid. Subsequent treatment of **5** with PPh_3 in CH_2Cl_2 afforded bisphosphine complex **6**.

The platinum complexes **3** and **6** were characterized by NMR spectroscopy (^1H (Table 1), $^{13}C\{^1H\}$, and ^{31}P) and elemental analysis. Remarkably high field shifts of the pendant OH groups were observed by ^1H NMR spectroscopy ($CDCl_3$, Table 1). These shifts can be

Table 1. Selected ^1H NMR Data[a,b] for 1−6

complex	H_{ortho}	aryl-H	CH_2N	NMe_2	OH
1		7.31, 7.26	3.40	2.20	3.06
2	7.92	7.11, 7.06	3.98	2.90	1.70
3	6.34	7.04, 7.82	3.96	2.97	0.68
4		7.29, 7.20	3.34	2.13	5.08
5	8.03	7.13, 6.99	3.94/3.91[c]	2.98/2.88	2.29
6	6.43	6.70, 5.90	4.02/3.98[c]	2.97/2.95	0.52

[a] 300 MHz, $CDCl_3$, δ in ppm. [b] Platinum and phosphorus couplings not included. [c] AB system.

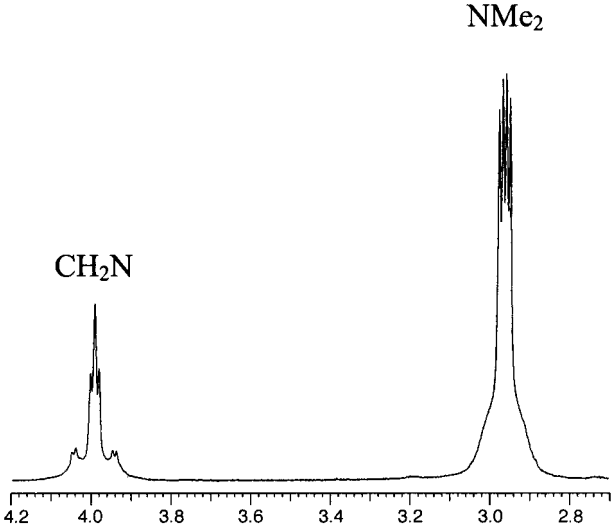


Figure 1. Part of the ^1H NMR spectrum of **6**, showing the resonances for the benzylic and NMe_2 protons.[11]

attributed to intramolecular interaction with the DMSO and PPh_3 ligands. Similar behavior was observed for the aryl protons of the platinum complexes, which also shifted to higher field with respect to the signals in the parent ligands.

For the bis-C,N complexes **5** and **6**, two resonances with platinum (and phosphorus for **6**) couplings were observed for the NMe_2 groups. The resonances for the protons on the benzylic positions (donor arms) were observed as AB patterns (Figure 1), which reflects the stereogenicity of the *para* substituent.[11] This pattern was observed not only for **5** and **6** but also for all complexes derived from **6** (see below). $^{195}Pt-^{31}P$ couplings of 4261 Hz (**3**) and 4281 Hz (**6**), respectively, were observed by $^{31}P\{^1H\}$ NMR spectroscopy. These data are consistent with the depicted structures of **3** and **6**, i.e., with the PPh_3 ligand *trans* to the nitrogen donor atom.

Compound **6** was further characterized by a single-crystal structure determination. The molecular structure of **6** in the solid state (Figure 2) comprises two platinum(II) metal centers, which each have a distorted square planar environment (Table 2), with C,N-bite angles of 80.8(2)° and 81.2(2)°. The substituents O(1) and H(10) at carbon atom C(10) are positionally disordered (pseudo-2-fold rotation axis). Only the major disorder component (54.7% occupancy) is shown in Figure 2. No hydrogen-bonding interaction was observed for **6** in the solid state between the C(H)OH and Pt−Cl groupings such as has been observed for the corresponding complexes [PtCl($C_6H_2\{CH_2NMe_2\}_2$-2,6-OH-4)][5] and [PtCl($C_6H_2\{CH_2NMe_2\}_2$-2,6-$\{CH_2OH\}$-4)].[12]

Derivatization of 3 and 6. The organometallic fragments **3** and **6** were prepared for use as precursors in the synthesis of larger macromolecular structures.

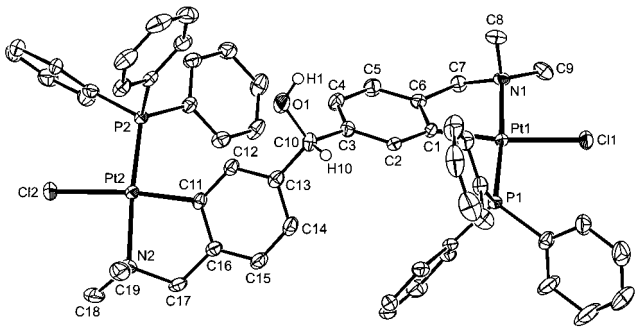


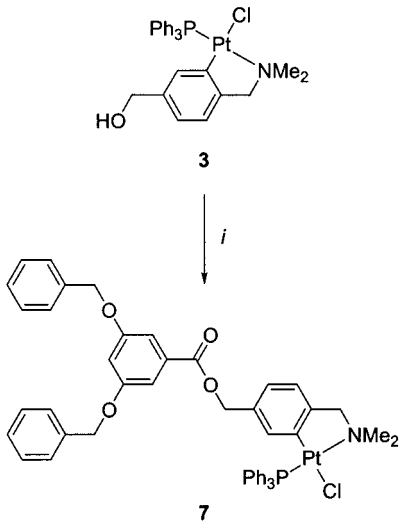
Figure 2. Displacement ellipsoid plot (50% probability level) of the molecular structure of **6**, with the adopted numbering scheme. All hydrogen atoms except H(1) and H(10) have been omitted for clarity. The substituents O(1) and H(10) at carbon atom C(10) are positionally disordered (pseudo-2-fold rotation axis). Only the major disorder component (54.7% occupancy) is shown.

Table 2. Selected Bond Distances (Å) and Angles (deg) of 6

Pt(1)−Cl(1)	2.3917(12)	Pt(2)−Cl(2)	2.3856(11)
Pt(1)−P(1)	2.2270(11)	Pt(2)−P(2)	2.2282(12)
Pt(1)−N(1)	2.143(4)	Pt(2)−N(2)	2.164(4)
Pt(1)−C(1)	2.025(4)	Pt(2)−C(2)	2.016(4)
Cl(1)−Pt(1)−P(1)	93.08(4)	Cl(2)−Pt(2)−P(2)	92.35(4)
Cl(1)−Pt(1)−N(1)	91.59(11)	Cl(2)−Pt(2)−N(2)	91.56(11)
P(1)−Pt(1)−C(1)	94.39(13)	P(2)−Pt(2)−C(11)	94.98(13)
N(1)−Pt(1)−C(1)	80.85(17)	N(2)−Pt(2)−C(11)	81.24(17)
P(1)−Pt(1)−N(1)	175.04(11)	P(2)−Pt(2)−N(2)	175.50(11)
Cl(1)−Pt(1)−C(1)	171.87(13)	Cl(2)−Pt(2)−C(11)	172.11(13)
interplanar angle	Pt(1)−Cl(1)−P(1) and Pt(1)−N(1)−C(1)		3.42(18)
	Pt(2)−Cl(2)−P(2) and Pt(1)−N(1)−C(1)		3.98(17)

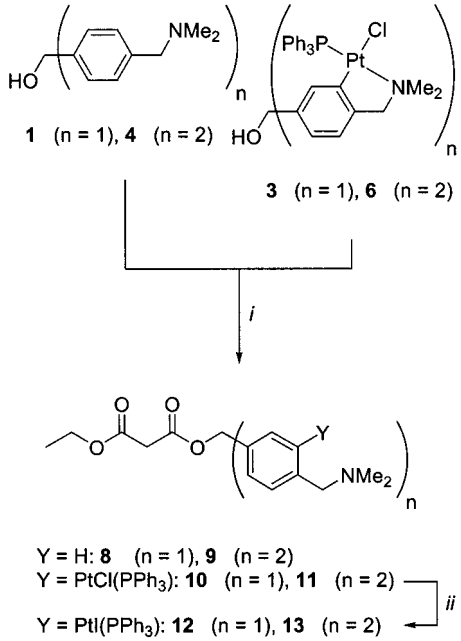
The pendant hydroxymethyl group in the platinum complexes **3** and **6** is well suited for direct reaction with acid chloride-substituted dendrimers or dendrons. Moreover, reaction with malonyl chloride enables coupling to C_{60} using the Bingel cyclopropanation reaction.[13] To demonstrate the use of C,N-platinum complexes in the synthesis of macromolecular structures based on dendrimers, the C,N-platinum complex **3** was attached to a small Fréchet type dendron/wedge.[14] Addition of [G1]-C(O)Cl to an equimolar amount of **3** in CH_2Cl_2 in the presence of base (NEt_3) yielded the dendritic platinum(II) complex **7** in 65% isolated yield (Scheme 3). Conclusive evidence for the formation of **7** was provided by the disappearance of the doublet resonance assigned to the benzylic protons of the hydroxymethyl group in **3** (δ = 3.96) and the appearance of a new singlet resonance at 4.62 ppm, attributed to the methylene group of the newly formed ester linkage. Furthermore, MALDI-TOF mass spectrometric analysis displayed the molecular ion peak $[M]^+$ and a $[M - Cl]^+$ peak for *m*/*z* 972.82 and 938.07, respectively. Similar $^{195}Pt-^{31}P$ coupling constants were observed for **3** (J = 4261 Hz) and for the [G1] dendrimer complex **7** (J = 4235 Hz). This

Scheme 3[a]



[a] Reagents and Conditions: (i) [G1]-C(O)Cl, NEt_3, CH_2Cl_2.

Scheme 4[a]



[a] Reagents and Conditions: (i) ethyl malonyl chloride, pyridine, or NEt_3, Et_2O, 0 °C; (ii) NaI, acetone.

suggests an unchanged spatial arrangement of the ligands about the platinum center. Moreover, the high-yield synthesis of **7** and its purity demonstrate the stability of the cycloplatinated C,N-building block.

Synthesis of Fullerene Derivatives. Methanofullerene C,N-platinum complexes are accessible via two routes: (a) preparation of the methanofullerene ligand followed by transmetalation, or (b) direct cyclopropanation of C_{60} with a malonate C,N-platinum complex. Both routes were studied for comparison. For this purpose, ethyl malonyl tails were attached not only to the C,N-platinum complexes **3** and **6** but also to the parent C,N-ligands **1** and **4**. Reaction of **1**, **3**, **4**, and **6** with ethyl malonyl chloride in Et_2O in the presence of base (NEt_3 or pyridine) at 0 °C afforded the corresponding malonate compounds **8**−**11** (Scheme 4). To avoid halogen scrambling (i.e, chloride−iodide exchange by I_2 during the Bingel reaction of the platinum−chloride

(11) Compounds **4**−**6** (and their derivatives) are interesting cases of an achiral $XYCR_2$ system where the C-center is prochiral, but any prochiral center in R is diastereotopic. For **4**, only singlets were observed by ^1H NMR, most likely due to a too small $\Delta\delta$ for the benzylic protons and NMe_2 groups.

(12) Slagt, M. Q.; van de Coevering, R.; Klein Gebbink, R. J. M.; Lutz, M.; Spek, A. L., van Koten, G., unpublished results.

(13) See for instance: (a) Bingel, C. *Chem. Ber.* **1993**, *126*, 1957. (b) Nierengarten, J.-F.; Felder, D.; Nicoud, J.-F. *Tetrahedron Lett.* **1998**, 2747, and references therein.

(14) (a) Hawker, C. J.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **1990**, *112*, 7638. (b) Wooley, K. L.; Hawker, C. J.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **1990**, *112*, 4253. (c) Albrecht, M.; Hovestad, N. J.; Boersma, J.; van Koten, G. *Chem. Eur. J.* **2001**, *7*, 1289.

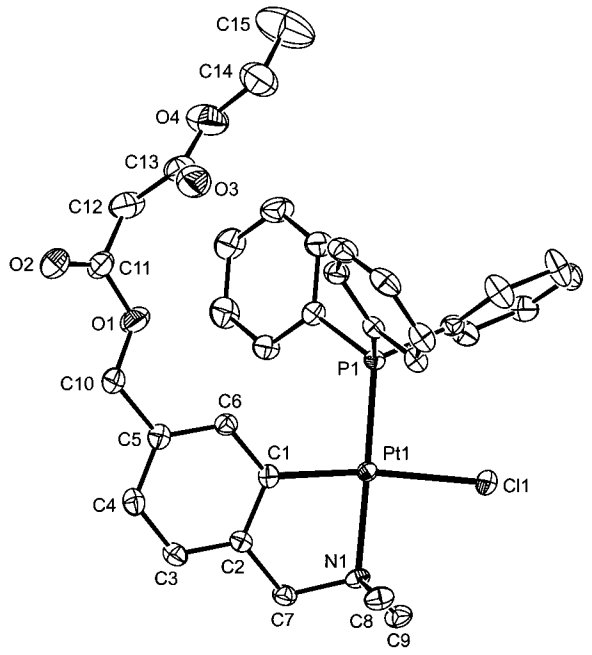


Figure 3. Displacement ellipsoid plot (50% probability level) of the molecular structure of **10**, with the adopted numbering scheme. The hydrogen atoms have been omitted for clarity.

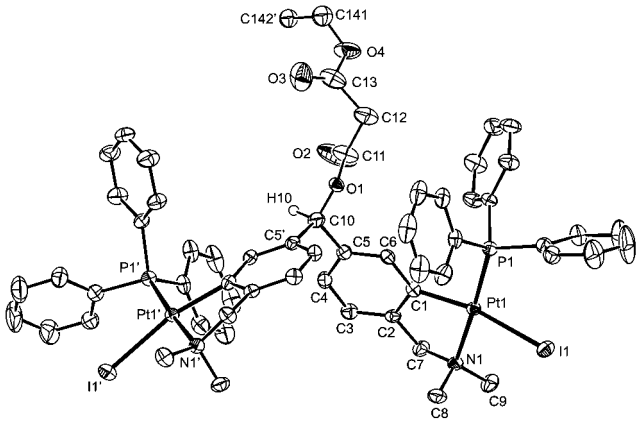


Figure 4. Displacement ellipsoid plot (50% probability level) of the molecular structure of **13**, with the adopted numbering scheme. All hydrogen atoms except H(10) have been omitted for clarity. The structure of **13** has an exact, crystallographic C_2 symmetry, leading to rotational disorder at carbon C(10) and disorder of the ethyl malonyl chain and the hydrogen atom H(10) (both in 50% occupancy, only one disorder component is shown).

complexes **10** and **11**), these complexes were converted into their corresponding iodide complexes **12** and **13** with NaI in acetone. The formation of these compounds was demonstrated by multinuclear NMR spectroscopy and elemental analysis. For **10** and **13**, the X-ray crystal structure was also determined.

The molecular plots of the structures of **10** and **13** in the solid state are shown in Figures 3 and 4, respectively, while a selection of bond lengths and bond angles is presented in Table 3. The structure of **13** has an exact, crystallographic C_2 symmetry axis, leading to rotational disorder at carbon C(10) and disorder of the ethyl malonyl chain and the hydrogen atom H(10) (both in 50% occupancy). Only one disorder component is shown in Figure 4 (symmetry operation: $1 - x, y, 0.5 - z$). The

Table 3. Selected Bond Distances (Å) and Angles (deg) of 10 and 13

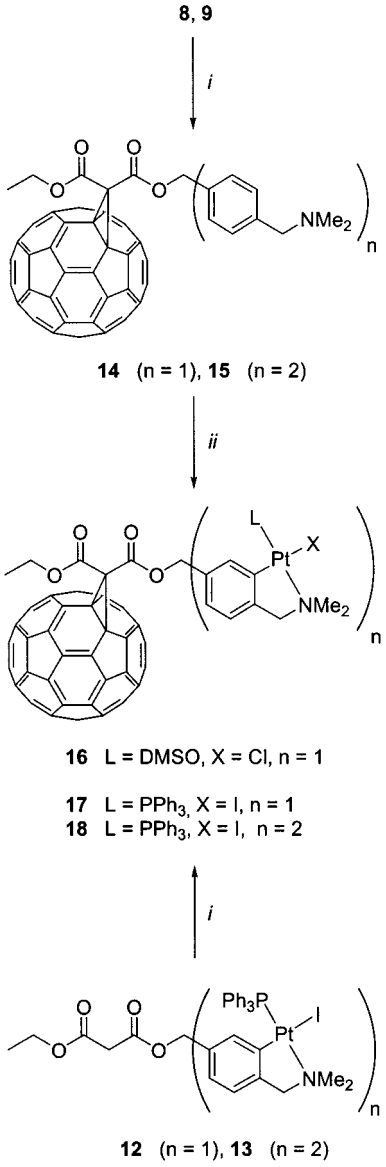
10		**13**	
Pt(1)−Cl(1)	2.3902(7)	Pt(1)−I(1)	2.6874(3)
Pt(1)−P(1)	2.2220(7)	Pt(1)−P(1)	2.2364(10)
Pt(1)−N(1)	2.138(2)	Pt(1)−N(1)	2.172(3)
Pt(1)−C(1)	2.008(3)	Pt(1)−C(1)	2.027(4)
Cl(1)−Pt(1)−P(1)	91.37(2)	I(1)−Pt(1)−P(1)	92.83(3)
Cl(1)−Pt(1)−N(1)	90.02(6)	I(1)−Pt(1)−N(1)	90.96(8)
P(1)−Pt(1)−C(1)	96.47(8)	P(1)−Pt(1)−C(1)	95.29(11)
N(1)−Pt(1)−C(1)	81.95(10)	N(1)−Pt(1)−C(1)	81.27(13)
P(1)−Pt(1)−N(1)	178.01(6)	P(1)−Pt(1)−N(1)	175.79(9)
Cl(1)−Pt(1)−C(1)	168.50(7)	I(1)−Pt(1)−C(1)	167.90(11)
interplanar angle between Pt(1)−Cl(1)−P(1) and Pt(1)−N(1)−C(1)	9.51(14)	interplanar angle between Pt(1)−I(1)−P(1) and Pt(1)−N(1)−C(1)	8.38(10)

platinum centers in both **10** and **13** have a distorted square planar coordination geometry, reflected by the C,N-bite angles of 81.95(8)° for **10** and 81.26(14)° for **13**, respectively. The ligand environment, i.e., the PPh_3 ligands positioned *trans* to the NMe_2 group and the chloride ligand *trans* to the aromatic ring, was not changed by the attachment of the malonyl group.

Derivatization of C_{60}. The malonates **8** and **9** were attached to C_{60} via a Bingel cyclopropanation reaction in the presence of I_2 and diazabicyclo[5.4.0]undec-7-ene (DBU) in toluene at room temperature (Scheme 5). The methanofullerenes **14** and **15** were characterized by NMR and mass spectroscopic analysis (MALDI-TOF). These methanofullerene CH,N ligands were reacted with *cis*-$PtCl_2(DMSO)_2$ and NaOAc in a mixture of MeOH and *ortho*-dichlorobenzene (ODCB, Scheme 5). Cycloplatination at the C,N-ligand took place for **14**, affording the platinum(II)-DMSO complex **16**, which was isolated in 57% yield. To our surprise, no bisplatinum complex starting from **15** was formed under the same conditions. Only starting material and insoluble products were isolated. However, direct attachment of the platinum complexes **12** and **13** to C_{60} in the presence of I_2 and DBU did yield the new methanofullerene C,N-platinum complexes **17** and **18**, respectively. Both **17** and **18** were isolated in reasonable yields (60% and 59% based on reacted C_{60}), which again demonstrates the stability of the C,N-platinum(II) building block. In the ^1H NMR spectrum of **17** and **18**, the methylene resonance of the malonyl group of the starting material had disappeared, indicating a complete reaction, while the expected methanofullerene resonances in the 150−120 ppm region were observed by $^{13}C\{^1H\}$ NMR spectroscopy. The $^{31}P-^{195}Pt$ coupling constants in the $^{31}P\{^1H\}$ NMR spectrum of 4167 Hz (**17**) and 4174 Hz (**18**) showed that the platinum center remained in the same coordination environment during the Bingel reaction. Mass spectrometric analysis (MALDI-TOF) exhibited fragments at *m*/*z* 1454.0 (**17**) and 2170.1 (**18**), corresponding to the respective $[M - I]^+$ fragments ions.

These results show that the chelated platinum center is stable under the conditions of the cyclopropanation reaction. Apparently, the formation of the α-halocarbanion and subsequent reaction with C_{60} is faster then the alternative Pt−C(C,N) bond cleavage. Moreover, we have found that the organometallic moiety of these complexes is also stable to the chromatographic workup conditions traditionally used in fullerene chemistry. Grafting of a complete organometallic synthon to C_{60} is thus a useful route for the synthesis of methanofullerene C,N-platinum(II) complexes, especially in cases where

Scheme 5. Derivatization of C_{60}[a]



[a] Reagents and Conditions: (i) C_{60}, I_2, DBU, toluene, rt, 24 h; (ii) *cis*-$PtCl_2(DMSO)_2$, NaOAc, MeOH/DCB (1:2 v/v %), 65 °C.

the methanofullerene ligand cannot be directly metalated. In summary, the presented C,N-platinum compounds have been shown to be versatile and stable complexes, suitable in dendrimer and fullerene chemistry. These complexes are also promising building blocks for other areas of macromolecular chemistry, e.g., for materials based on the use of metal d^8 complexes.[2]

Experimental Section

General Comments. All experiments were conducted under a dry dinitrogen atmosphere using standard Schlenk techniques. Solvents were dried over appropriate materials and distilled prior to use. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded at 298 K (unless stated otherwise) on a Varian Inova 300 MHz spectrometer, $^{31}P\{^1H\}$ NMR spectra were recorded on a Varian Mercury 200 MHz NMR spectrometer. All NMR chemical shifts are in ppm referenced to residual solvent signals (^1H and $^{13}C\{^1H\}$) or to H_3PO_4 ($^{31}P\{^1H\}$). The starting materials *cis*-$PtCl_2(DMSO)_2$,[15] 4-[(dimethylamino)methyl]bromobenzene,[6] 4-[(dimethylamino)methyl]benzaldehyde,[16] and the Fréchet dendron [G1]-COCl[14] were prepared according to literature procedures. C_{60} (Hoechst, Gold Grade) was used as received. The MALDI-TOF mass spectra were acquired using a Voyager-DE BioSpectrometry Workstation mass spectrometer (PerSeptive Biosystems Inc., Framingham, MA). Sample solutions with an approximate concentration of 1 g L^{-1} in CH_2Cl_2 were prepared. The matrix was 9-nitroanthracene (9-NA) with an approximate concentration of 40−50 g L^{-1}. An 0.2 μL aliquot of the sample solution and 0.2 μL of the matrix solution were combined on a golden MALDI target and analyzed after evaporation of the solvent. Elemental analyses were performed by Dornis und Kolbe, Mikroanalytisches Laboratorium (Mülheim, Germany).

4-[(Dimethylamino)methyl]benzyl Alcohol (1). To a suspension of $LiAlH_4$ (3.27 g, 86.2 mmol) in Et_2O (75 mL) at 0 °C was added a solution of 4-[(dimethylamino)methyl]benzaldehyde (7.03 g, 43.1 mmol) in Et_2O (40 mL). The reaction mixture was stirred for 20 h, carefully quenched with 10 mL of a saturated aqueous solution of NaCl, and filtered. The organic fraction was separated, dried over $MgSO_4$, filtered, and evaporated in vacuo to yield **1** as a colorless oil (4.97 g, 77%). ^1H NMR ($CDCl_3$): δ 7.31 (d, 2H, ^3J = 8.7 Hz, Ar-*H*), 7.26 (d, 2H, ^3J = 8.4 Hz, Ar-*H*), 4.65 (s, 2H, CH_2OH), 3.40 (s, 2H, CH_2N), 3.06 (s, 1H, O*H*), 2.20 (s, 6H, NCH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 140.1, 137.6, 129.3, 126.9 (aryl-*C*), 64.9 (*C*OH), 64.0 (*C*H_2N), 45.1 (N*C*H_3). Anal. Calcd for $C_{10}H_{15}NO$: C 72.69, H 9.15, N 8.48. Found: C 72.56, H 9.21, N 8.44.

3-[Chloro(DMSO)platino]-4-[(dimethylamino)methyl]-benzyl Alcohol (2). To a solution of **1** (1.06 g, 6.42 mmol) in MeOH (40 mL) was added *cis*-$PtCl_2(DMSO)_2$ (2.77 g, 6.55 mmol) and NaOAc (0.54 g, 6.6 mmol). The reaction mixture was stirred at 65 °C for 3 h, whereupon a white solid separated from the solution. The product was collected by decantation, washed with MeOH (50 mL) and Et_2O (2 × 50 mL), and dried in vacuo, yielding **2** as a white solid (2.00 g, 66%). ^1H NMR ($CDCl_3$): δ 7.92 (s, ^3J(Pt−H) = 47.4 Hz, 1H, Ar-H_{ortho}), 7.11 (d, ^2J = 7.80 Hz, 1H, Ar-*H*), 7.06 (d, ^2J = 7.80 Hz, 1H, Ar-*H*), 4.64 (d, ^2J = 6.0 Hz, 2H, CH_2O), 3.98 (s, ^3J(Pt−H) = 39.9 Hz, 2H, CH_2N), 3.54 (s, ^3J(Pt−H) = 24.9 Hz, 6H, SCH_3), 2.90 (s, ^3J(Pt−H) = 33.9 Hz, 6H, NCH_3), 1.70 (t, ^2J = 6.0 Hz, 1H, O*H*). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 145.5, 138.7 (^3J(Pt−C) = 53.3 Hz), 136.2 (^1J(Pt−C) = 1061.3 Hz, Ar-C_{ipso}), 132.9 (^2J(Pt−C) = 54.0 Hz), 123.9, 121.8 (^3J(Pt−C) = 36.4 Hz), 74.7 (^2J(Pt−C) = 51.5 Hz, *C*H_2N), 65.8 (*C*OH), 52.2 (N*C*H_3), 46,8 (^2J(Pt−C) = 63.1 Hz, S*C*H_3). Anal. Calcd for $C_{12}H_{20}ClNO_2PtS$: C 30.48, H 4.26, N 2.96. Found: C 30.34, H 4.21, N 2.85.

3-[Chloro(triphenylphosphine)platino]-4-[(dimethylamino)methyl]benzyl Alcohol (3). To a suspension of **2** (1.01 g, 2.14 mmol) in CH_2Cl_2 (40 mL) was added PPh_3 (0.59 g, 2.2 mmol). The reaction mixture was stirred for 2 h, filtered through Celite, and evaporated in vacuo. The crude product was washed with Et_2O (2 × 50 mL) and dried in vacuo, yielding **3** as a white solid (0.90 g, 64%). ^1H NMR ($CDCl_3$): δ 7.79−7.72 (m, 6H, PAr-*H*), 7.44−7.32 (m, 9H, PAr-*H*), 7.04 (d, ^3J = 7.2 Hz, 1H, Ar-*H*), 6.82 (dd, ^3J = 7.7 Hz, ^4J = 1.8 Hz, 1H, Ar-*H*), 6.34 (dd, ^3J(Pt−H) = 56.7 Hz, ^4J(P−H) = 2.6 Hz, ^4J = 1.8 Hz, 1H, Ar-H_{ortho}), 4.06 (d, ^3J(Pt−H) = 29.7 Hz, ^3J(P−H) = 3.0 Hz, 2H, CH_2N), 3.96 (d, ^3J = 6.0 Hz, 2H, CH_2O), 2.97 (d, ^3J(Pt−H) = 24.3 Hz, ^3J(P−H) = 3.3 Hz, 6H, NCH_3), 0.68 (t, ^3J = 6.0 Hz, 1H, O*H*). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 146.91 (Ar-*C*), 138.04 (d, ^1J(P−C) = 6.7 Hz, PAr-C_{ipso}), 137.57 (d, ^2J(P−C) = 2.4 Hz, Ar-*C*), 135.29 (d, ^2J(P−C) = 10.4 Hz, ^3J(Pt−C) = 39.5 Hz, PAr-C_{ortho}), 130.77 (Ar-*C*), 130.55 (d, ^4J(P−C) = 2.4 Hz, Ar-C_{para}), 129.95 (^3J(Pt−C) = 36.3 Hz, Ar-*C*), 127.82 (d, ^3J(P−C) = 10.9 Hz, PAr-C_{meta}), 121.93 (Ar-*C*), 121.66 (^3J(Pt−C) = 35.3 Hz, Ar-*C*), 74.0 (^2J(Pt−C) = 50.3 Hz, *C*H_2N), 65.3 (*C*OH), 50.7 (N*C*H_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 20.7 (^1J(Pt−P) = 4261 Hz). Anal. Calcd for $C_{28}H_{29}ClNOPPt$: C 51.18, H 4.45, N 2.13. Found: C 51.18, H 4.55, N 2.04.

(15) Price, J. H.; Williamson, A. N.; Schramm, R. F.; Wayland, B. B. *Inorg. Chem.* **1972**, *11*, 1280.
(16) Meijer, M. D.; de Wolf, E.; Lutz, M.; Spek, A. L.; van Klink, G. P. M.; van Koten, G. *Organometallics* **2001**, *20*, 4198.

Bis(4-[(dimethylamino)methyl]phenyl)methyl Alcohol (4). To a solution of 4-[(dimethylamino)methyl]bromobenzene (5.80 g, 27.1 mmol) in Et_2O (30 mL) at −78 °C was added 37 mL of a 1.5 M solution of *t*-BuLi in pentane (55 mmol). The reaction mixture was stirred at −78 °C for 1 h, and a solution of 4-[(dimethylamino)methyl]benzaldehyde (4.43 g, 27.1 mmol) in Et_2O (25 mL) was added in one portion. The reaction mixture was allowed to warm to room temperature over 2 h and was quenched with water (50 mL). The organic layer was separated, and the water layer extracted with Et_2O (2 × 100 mL). The organic fractions were dried on $MgSO_4$, filtered, and evaporated in vacuo. The crude product was purified using Kugelrohr distillation giving **4** as a yellow oil, which solidified upon standing (6.23 g, 77%). ^{1}H NMR ($CDCl_3$): δ 7.29 (d, 4H, ^3J = 8.4 Hz, Ar-*H*), 7.20 (d, 4H, ^3J = 8.1 Hz, Ar-*H*), 5.71 (s, 1H, C*H*O), 5.08 (s, 1H, O*H*), 3.34 (s, 4H, CH_2N), 2.13 (s, 12H, NCH_3). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 143.5, 137.0, 129.2, 126.4 (Ar-*C*), 75.4 (*C*OH), 63.8 (*C*H_2N), 45.0 (N*C*H_3). Anal. Calcd for $C_{19}H_{26}N_2O$: C 76.47, H 8.78, N 9.39. Found: C 76.29, H 8.90, N 9.26.

Bis(3-[chloro (DMSO) platino]-4-[(dimethylamino)-methyl]phenyl)methyl Alcohol (5). Complex **5** was synthesized using the same method as that described for **2** starting from **4** (0.35 g, 1.2 mmol), *cis*-$PtCl_2(DMSO)_2$ (1.01 g, 2.39 mmol), and NaOAc (0.21 g, 2.6 mmol). Complex **5** was isolated as a white solid (0.91 g, 84%). ^{1}H NMR ($CDCl_3$): δ 8.03 (d, ^3J(Pt−H) = 48.0 Hz, ^4J = 1.2 Hz, 2H, Ar-H_{ortho}), 7.13 (dd, ^3J = 7.5 Hz, ^4J = 1.2 Hz, 2H, Ar−H), 6.99 (d, ^3J = 8.1 Hz, 2H, Ar−H), 5.77 (d, ^3J = 3.0 Hz, 1H, C*H*O), 3.94/3.91 (dd, AB, ^2J = 13.7 Hz, ^3J(Pt−H) = 36.9 Hz, 4H, CH_2N), 3.50 (s, ^3J(Pt−H) = 21.6 Hz, 12H, SCH_3), 2.89, 2.88 (2 × s, ^3J(Pt−H) = 31.5 Hz, 12H, NCH_3), 2.29 (d, ^3J = 3.3 Hz, 1H, *H*OCH). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 145.0 (^4J(Pt−C) = 18.2 Hz), 142.5, 136.3, 132.5 (^2J(Pt−C) = 55.2 Hz, Ar-*C*), 123.3 (Ar-*C*), 121.9 (^3J(Pt−C) = 37.7 Hz, Ar-*C*), 77.1 (*C*OH), 74.9 (^2J(Pt−C) = 53.0 Hz, *C*H_2N), 52.43, 52.38 (N*C*H_3), 47.0 (^2J(Pt−C) = 64.9 Hz, S*C*H_3). Anal. Calcd for $C_{23}H_{36}Cl_2N_2O_3Pt_2S_2$: C 53.79, H 7.05, N 7.84. Found: C 53.88, H 7.11, N 7.86.

Bis(3-[chloro(triphenylphosphine)platino]-4-[(dimethylamino)methyl]phenyl)methyl Alcohol (6). Complex **6** was synthesized using the same method as that described for **3** starting from **5** (0.47 g, 0.51 mmol) and PPh_3 (0.27 g, 1.0 mmol), yielding **6** as a white solid (0.52 g, 80%). ^{1}H NMR ($CDCl_3$): δ 7.75−7.67 (m, 12H, PAr-*H*), 7.42−7.29 (m, 18H, PAr-*H*), 6.70 (d, ^3J = 7.5 Hz, 2H, Ar-*H*), 6.43 (dd, ^3J(Pt−H) = 57.3 Hz, ^4J(P−H) = 2.9 Hz, ^4J = 1.3 Hz, 2H, Ar-H_{ortho}), 5.90 (dd, ^3J = 7.7 Hz, ^4J = 1.3 Hz, 2H, Ar-*H*), 4.35 (d, ^3J = 3.6 Hz, 1H, C*H*O), 4.02/3.98 (dd, AB, ^2J = 13.7 Hz, ^4J(P−H) = 3.0 Hz, ^3J(Pt−H) = 30.5 Hz, 4H, CH_2N), 2.97, 2.95 (2 × d, ^4J(P−H) = 2.7 Hz, ^3J(Pt−H) not resolved, 12H, NCH_3), 0.52 (d, ^3J = 3.6 Hz, 1H, O*H*). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 146.0 (Ar-*C*), 140.68 (d, ^2J(P−C) = 2.3 Hz, Ar-*C*), 136.84 (d, ^1J(P−C) = 6.8 Hz, PAr-C_{ipso}), 135.18 (d, ^2J(P−C) = 11.0 Hz, PAr-C_{ortho}), 130.89 (Ar-*C*), 130.41 (d, ^4J(P−C) = 2.4 Hz, PAr-C_{para}), 130.08 (Ar-*C*), 127.78 (d, ^3J(P−C) = 11.0 Hz, PAr-C_{meta}), 121.15 (Ar-*C*), 120.95 (Ar-*C*), 76.2 (*C*OH), 74.1 (^2J(Pt−C) = 52.5 Hz, *C*H_2N), 50.9, 50.7 (N*C*H_3). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 21.1 (^1J(Pt−P) = 4281 Hz). Anal. Calcd for $C_{55}H_{54}Cl_2N_2OP_2Pt_2$: C 51.53, H 4.25, N 2.19. Found: C 51.34, H 4.30, N 2.20.

{3-[Chloro(triphenylposphine)platino]-4-[(dimethylamino)methyl]benzyl}-[G1]-carboxylate (7). To a solution of **4** (0.67 g, 1.0 mmol) in CH_2Cl_2 (25 mL) was added NEt_3 (0.20 mL, 1.4 mmol). A solution of the Fréchet dendron [G1]-C(O)Cl (0.36 g, 1.0 mmol) in CH_2Cl_2 (25 mL) was added dropwisely, and the solution was stirred at room temperature for 3 days. The reaction mixture was washed with an aqeous saturated NaCl solution (50 mL), dried over $MgSO_4$, filtered, and evaporated in vacuo. The remaining solid was washed with Et_2O (2 × 15 mL) and dried in vacuo, yielding **7** as a white solid (0.65 g, 65%). ^{1}H NMR ($CDCl_3$): δ 7.76−7.68 (m, 6H, Ar-*H*), 7.46−7.27 (m, 19H, Ar-*H*), 7.13 (d, ^4J = 2.5 Hz, 2H, Ar-*H*), 7.04 (d, ^3J = 7.8 Hz, 1H, Ar-*H*), 6.92 (dd, ^3J = 7.4 Hz, ^4J = 1.6 Hz, 1H, Ar-*H*), 6.80 (t, ^4J = 2.4 Hz, 1H, Ar−H), 6.43 (dd, ^3J(Pt−H) = 52.8 Hz, ^4J(P−H) = 3.0 Hz, ^4J = 1.5 Hz, 2H, Ar-H_{ortho}), 5.06 (s, 4H, CH_2O), 4.62 (s, 2H, CH_2O), 4.07 (d, ^3J(Pt−H) = 27.1 Hz, ^3J(P−H) = 3.0 Hz, 2H, CH_2N), 2.99 (d, ^3J(Pt−H) = 23.4 Hz, ^3J(P−H) = 2.8 Hz, 6H, NCH_3). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 165.74, 159.60, 147.53 (Ar-*C*), 137.63 (^1J(P−C) = 7.1 Hz, PAr-C_{ipso}), 137.48 (^2J(Pt−C) = 86.7 Hz, Ar-*C*), 136.40, 135.15 (d, ^2J(P−C) = 10.9 Hz, PAr-C_{ortho}), 132.22 (^2J(Pt−C) = 72.3 Hz, Ar-*C*), 132.11 (Ar-*C*), 130.54 (PAr-C_{para}), 129.77 (^4J(Pt−C) = 31.5 Hz, Ar-*C*), 128.63, 128.16, 128.03, 127.75 (d, ^3J(P−C) = 10.9 Hz, PAr-C_{meta}), 127.58, 123.13 (Ar-*C*), 121.57 (^4J(Pt−C) = 32.2 Hz, Ar-*C*), 108.73, 106.43, 74.1 (^2J(Pt−C) = 51.0 Hz, *C*H_2N), 70.3 (O*C*H_2), 67.0 (O*C*H_2), 50.8 (N*C*H_3). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 20.9 (^1J(Pt−P) = 4235 Hz). MALDI-TOF (9-NA): *m*/*z* 972.82 [M]$^+$, 938.07 [M − Cl]$^+$. Anal. Calcd for $C_{49}H_{45}ClNO_4PPt$: C 60.46, H 4.66, N 1.44. Found: C 60.34, H 4.58, N 1.43.

1-{4′-[(Dimethylamino)methyl]benzyl}-3-ethylmalonate (8). To a solution of **1** (1.50 g, 9.07 mmol) in CH_2Cl_2 (40 mL) at −60 °C was added pyridine (0.77 mL, 9.5 mmol). A solution of ethyl malonyl chloride (1.2 mL, 9.5 mmol) in CH_2Cl_2 (25 mL) was added dropwise, and the solution was allowed to warm overnight. The solution was washed with a saturated solution of $NaHCO_3$ (3 × 60 mL), dried on $MgSO_4$, filtered, and evaporated in vacuo, yielding **8** as a yellow oil (2.03 g, 80%). ^{1}H NMR ($CDCl_3$): δ 7.26 (s, 4H, Ar-*H*), 5.12 (s, 2H, OCH_2), 4.13 (q, ^3J = 7.5 Hz, 2H, OEt), 3.37 (s, 2H, CH_2N), 3.36 (s, 2H, C(O)CH_2C(O)), 2.18 (s, 6H, NCH_3), 1.19 (t, ^3J = 6.9 Hz, 3H, OEt). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 166.2, 166.1 (*C*O), 139.0, 133.9, 129.0, 128.0 (Ar-*C*), 66.7 (O*C*H_2), 63.7 (*C*H_2N), 61.2 (OEt), 45.1 (N*C*H_3), 41.3 (C(O)*C*H_2C(O)), 13.8 (OEt). Anal. Calcd for $C_{15}H_{21}NO_4$: C 64.50, H 7.58, N 5.01. Found: C 64.43, H 7.51, N 5.05.

1-[Bis(4-[(dimethylamino)methyl]phenyl)methyl]-3-ethylmalonate (9). To a solution of ethyl malonyl chloride (0.80 mL, 6.6 mmol) in CH_2Cl_2 (40 mL) was added a solution of **4** (0.96 g, 3.2 mmol) in CH_2Cl_2 (30 mL). The reaction mixture was stirred for 3 h and evaporated in vacuo. The remaining white solid was washed with Et_2O (4 × 50 mL) and suspended in CH_2Cl_2 (50 mL). Then NEt_3 (3 mL) was added to the mixture, upon which the mixture clarified. This was washed with a saturated $NaHCO_3$ solution (2 × 50 mL) and an aqeous saturated NaCl solution (50 mL). The organic solution was dried on $MgSO_4$, filtered, and evaporated in vacuo, yielding **9** as a yellow oil (0.82 g, 62%). ^{1}H NMR ($CDCl_3$): δ 7.23 (s, 8H, Ar-*H*), 6.87 (s, C*H*), 4.11 (q, ^3J = 6.9 Hz, 2H, OEt), 3.39 (s, 2H, C(O)CH_2C(O)), 3.29 (s, 4H, CH_2N), 2.15 (s, 12H, NCH_3), 1.15 (t, ^3J = 7.2 Hz, 3H, OEt). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 165.9, 165.2 (*C*O), 138.5, 138.1, 128.7, 126.7 (Ar-*C*), 77.3 (O*C*H), 63.6 (*C*H_2N), 61.1 (OEt), 45.0 (N*C*H_3), 41.5 (C(O)*C*H_2C(O)), 13.7 (OEt). Anal. Calcd for $C_{24}H_{32}N_2O_4$: C 69.88, H 7.82, N 6.79. Found: C 70.05, H 7.94, N 6.82.

1-{3′-[Chloro(triphenylposphine)platino]-4′-[(dimethylamino)methyl]benzyl}-3-ethylmalonate (10). To a solution of **3** (1.26 g, 1.92 mmol) in CH_2Cl_2 (40 mL) at 0 °C was added NEt_3 (0.40 mL, 2.9 mmol) and ethyl malonyl chloride (0.37 mL, 2.9 mmol). The reaction mixture was stirred for 5 h and evaporated in vacuo. The remaining white solid was washed with Et_2O (3 × 40 mL) and dissolved in CH_2Cl_2. The solution was washed with a saturated solution of $NaHCO_3$ (2 × 40 mL) and a saturated solution of NaCl (2 × 40 mL), dried on $MgSO_4$, and evaporated in vacuo, yielding **10** as a white solid (0.80 g, 54%). ^{1}H NMR ($CDCl_3$): δ 7.77−7.67 (m, 6H, PAr-*H*), 7.43−7.31 (m, 9H, PAr-*H*), 7.01 (d, ^3J = 7.5 Hz, 1H, Ar-*H*), 6.82 (dd, ^3J = 7.5 Hz, ^4J = 1.5 Hz, 1H, Ar-*H*), 6.35 (dd, ^3J(Pt−H) = 56.7 Hz, ^4J(P−H) = 2.7 Hz, ^4J = 1.8 Hz, 1H, Ar-H_{ortho}), 4.48 (s, 2H, OCH_2), 4.17 (q, 2H, ^3J = 7.3 Hz), 4.05 (d, ^3J(Pt−H) = 28.4 Hz, ^3J(P−H) = 2.8 Hz, 2H, CH_2N), 3.12 (s, 2H, C(O)CH_2C-(O)), 2.97 (d, ^3J(Pt−H) = 23.8 Hz, ^3J(P−H) = 2.7 Hz, 6H, NCH_3), 1.22 (t, ^3J = 6.8 Hz). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 147.66

(Ar-*C*), 137.38 (d, ^1J(P−C) = 6.1 Hz, PAr-C_{ipso}), 135.18 (d, ^2J(P−C) = 11.0 Hz, Ar-C_{ortho}), 131.61 (d, ^2J(P−C) = 2.5 Hz, Ar-*C*), 130.64 (Ar-*C*), 130.53 (d, ^4J(P−C) = 2.4 Hz, PAr-C_{para}), 129.82, 127.81 (d, ^3J(P−C) = 11.0 Hz, PAr-C_{meta}), 122.91 (Ar-*C*), 121.56 (Ar-*C*), 74.0 (^2J(Pt−C) = 56.3 Hz, *C*H_2N), 67.2 (O*C*H_2), 61.4 (OEt), 50.8 (N*C*H_3), 41.3 (C(O)*C*H_2C(O)), 14.0 (OEt). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 21.2 (^1J(Pt−P) = 4236 Hz). Anal. Calcd for $C_{33}H_{35}ClNO_4PPt$: C 51.40, H 4.57, N 1.82. Found: C 51.24, H 4.65, N 1.74.

1-{Bis(3′-[chloro(triphenylposphine)platino]-4′-[(dimethylamino)methyl]phenyl)methyl}-3-ethylmalonate (11). Compound **11** was prepared using the same method as for **10** starting from **6** (2.28 g, 1.78 mmol), ethyl malonyl chloride (0.34 mL, 2.7 mmol), and NEt_3 (0.37 mL, 2.7 mmol), yielding **11** as a white solid (1.90 g, 76%). ^{1}H NMR ($CDCl_3$): δ 7.71−7.65 (m, 12H, PAr-*H*), 7.43−7.26 (m, 18H, PAr-*H*), 6.67 (d, ^3J = 7.5 Hz, 2H, Ar-*H*), 6.39 (^3J(Pt−H) = 55.2 Hz, 2H, Ar-H_{ortho}), 5.79 (dd, ^3J = 7.8 Hz, ^4J = 0.9 Hz, 2H, Ar-*H*), 5.47 (s, 1H, OC*H*), 4.08 (q, 2H, ^3J = 6.9 Hz, OEt), 4.01/3.95 (dd, AB, ^3J = 13.5 Hz, ^3J(P−H) = 2.7 Hz, 4H, CH_2N), 2.96, 2.93 (2 × d, ^3J(P−H) = 2.7 Hz, 12H, NCH_3), 2.46 (s, 2H, C(O)CH_2C(O)), 1.15 (t, ^3J = 6.9 Hz, OEt). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 146.47 (Ar-*C*), 136.64 (d, ^1J(P−C) = 6.7 Hz, PAr-C_{ipso}), 136.47 (d, ^2J(P−C) = 2.4 Hz, Ar-*C*), 135.12 (d, ^4J(P−C) = 10.9 Hz, PAr-C_{ortho}), 130.8 (Ar-*C*), 130.46 (d, ^4J(P−C) = 1.8 Hz, Ar-C_{para}), 130.03 (Ar-*C*), 127.80 (d, ^3J(P−C) = 11.6 Hz, PAr-C_{meta}), 121.63 (Ar-*C*), 121.29 (Ar-*C*), 77.8 (O*C*H), 74.1 (^2J(Pt−C) = 49.7 Hz, *C*H_2N), 61.1 (OEt), 50.9, 50.8 (N*C*H_3), 40.8 (C(O)*C*H_2C(O)), 14.0 (OEt). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 21.6 (^1J(Pt−P) = 4262 Hz). Anal. Calcd for $C_{60}H_{60}Cl_2N_2O_4P_2Pt_2$: C 51.62, H 4.33, N 2.01. Found: C 51.69, H 4.28, N 1.97.

1-{4′-[(Dimethylamino)methyl]-3′-[iodo(triphenylposphine)platino]benzyl}-3-ethylmalonate (12). To a solution of **10** (0.44 g, 0.57 mmol) in acetone (25 mL) was added NaI (0.85 g, 4.4 mmol). The reaction mixture was stirred for 2 h and evaporated in vacuo. The resultant white solid was extracted with CH_2Cl_2 (20 mL). Hexanes (60 mL) were added to the solution, whereupon a precipitate was formed. This was isolated and dried in vacuo, giving **12** as a tan solid (0.40 g, 81%). ^{1}H NMR ($CDCl_3$): δ 7.77−7.69 (m, 6H, PAr-*H*), 7.44−7.31 (m, 9H, PAr-*H*), 7.02 (d, ^3J = 7.5 Hz, 1H, Ar-*H*), 6.86 (dd, ^3J = 7.8 Hz, ^4J = 1.8 Hz, 1H, Ar-*H*), 6.35 (dd, ^3J(Pt−H) = 58.2 Hz, ^4J(P−H) = 3.6 Hz, ^4J = 1.5 Hz, 1H, Ar-H_{ortho}), 4.48 (s, 2H, O*C*H_2), 4.17 (q, 2H, ^3J = 6.9 Hz), 4.09 (d, ^3J(Pt−H) = 24.0 Hz, ^3J(P−H) = 2.4 Hz, 2H, CH_2N), 3.15 (d, ^3J(Pt−H) = 24.6 Hz, ^3J(P−H) = 3.0 Hz, 6H, NCH_3), 3.12 (s, 2H, C(O)CH_2C(O)), 1.23 (t, ^3J = 6.9 Hz, OEt). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 147.64 (Ar-*C*), 136.35 (d, ^1J(P−C) = 6.7 Hz, PAr-C_{ipso}), 135.31 (d, ^2J(P−C) = 10.4 Hz, Ar-C_{ortho}), 132.28 (Ar−C), 131.62 (d, ^4J(P−C) = 2.5 Hz, Ar-*C*), 130.46 (Ar-*C*), 130.60 (d, ^4J(P−C) = 3.3 Hz, Ar-C_{para}), 127.76 (d, ^3J(P−C) = 11.5 Hz, PAr-C_{meta}), 123.14 (Ar-*C*), 121.80 (^3J(Pt−C) = 32.8 Hz, Ar-*C*), 74.2 (^2J(Pt−C) = 53.4 Hz, *C*H_2N), 67.2 (O*C*H_2), 61.5 (OEt), 53.2 (N*C*H_3), 41.4 (C(O)*C*H_2C(O)), 14.1 (OEt). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 19.7 (^1J(Pt−P) = 4189 Hz). Anal. Calcd for $C_{33}H_{35}INO_4PPt$: C 45.95, H 4.09, N 1.62. Found: C 45.80, H 3.98, N 1.58.

1-{Bis(4′-[(dimethylamino)methyl]-3′-[iodo(triphenylposphine)platino]phenyl)methyl}-3-ethylmalonate (13). To a solution of **11** (1.43 g, 1.02 mmol) in acetone (50 mL) was added NaI (1.5 g, 10 mmol). The reaction mixture was stirred for 2 h and evaporated in vacuo, and the remaining solid was extracted with CH_2Cl_2 (50 mL). This was evaporated in vacuo, yielding **13** as a tan solid (1.38 g, 86%). ^{1}H NMR ($CDCl_3$): δ 7.72−7.63 (m, 12H, PAr-*H*), 7.38−7.27 (m, 18H, PAr-*H*), 6.68 (d, ^3J = 7.8 Hz, 2H, Ar-*H*), 6.39 (dd, ^3J(Pt−H) = 59.8 Hz, ^4J(P−H) = 3.5 Hz, ^4J = 1.2 Hz, 2H, Ar-H_{ortho}), 5.70 (dd, ^3J = 7.6 Hz, ^4J = 1.2 Hz, 2H, Ar-*H*), 5.52 (s, 1H, OC*H*), 4.08 (q, 2H, ^3J = 7.5 Hz, OEt), 4.05/3.99 (dd, AB, ^3J = 13.4 Hz, ^3J(P−H) = 3.0 Hz, 4H, CH_2N), 3.15, 3.09 (2 × d, ^3J(P−H) = 2.7 Hz, 12H, NCH_3), 2.52 (s, 2H, C(O)CH_2C(O)), 1.15 (t, ^3J = 6.9 Hz, OEt). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 166.04, 164.43 (*C*O), 146.45 (Ar-*C*), 136.22 (d, ^2J(P−C) = 2.4 Hz, Ar-*C*), 135.13 (d, ^4J(P−C) = 11.0 Hz, PAr-C_{ortho}), 136.64 (d, ^1J(P−C) = 6.7 Hz, PAr-C_{ipso}), 132.4 (^3J(Pt−C) = 29.0 Hz, Ar-*C*), 131.67 (^3J(Pt−C) = 30.4 Hz, Ar-*C*), 130.34 (PAr-C_{para}), 127.69 (d, ^3J(P−C) = 10.9 Hz, PAr-C_{meta}), 121.85 (Ar-*C*), 121.14 (Ar-*C*), 74.1 (^2J(Pt−C) = 46.7 Hz, *C*H_2N), 61.1 (OEt), 53.3, 52.9 (N*C*H_3), 40.9 (C(O)*C*H_2C(O)), 14.0 (OEt). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 20.0 (^1J(Pt−P) = 4202 Hz). Anal. Calcd for $C_{60}H_{60}I_2N_2O_4P_2Pt_2$: C 45.64, H 3.83, N 1.77. Found: C 45.88, H 3.76, N 1.85.

1,2-Dihydro-61-ethoxycarbonyl-61-{4-[(dimethylamino)methyl]benzyloxycarbonyl}-1,2-methano[60]fullerene (14). To a solution of **8** (0.38 g, 1.3 mmol), C_{60} (0.91 g, 1.3 mmol), and I_2 (0.65 g, 2.5 mmol) in toluene (900 mL) was added dropwise DBU (1.1 mL, 7.1 mmol). The reaction mixture was stirred for 17 h and poured on top of a silica gel column. Elution with toluene afforded 0.20 g of unreacted C_{60}. Elution with toluene/MeOH (95:5 v/v %) gave the crude product after evaporation of the solvent. This was dissolved in CS_2 (10 mL) and pentane was added (75 mL), whereupon the product precipitated. This procedure was repeated and the precipitate dried in vacuo, yielding **14** as a light brown solid (0.44 g, 35%, 45% based on reacted C_{60}). ^{1}H NMR (CS_2/C_6D_6, 3:1 v/v %): δ 7.23 (d, ^3J = 8.4 Hz, 2H, Ar-*H*), 7.21 (d, ^3J = 8.4 Hz, 2H, Ar-*H*), 5.25 (s, 2H, O*C*H_2), 4.21 (q, ^3J = 7.2 Hz, 2H, OEt), 3.27 (s, 2H, CH_2N), 2.09 (s, 6H, NCH_3), 1.14 (t, ^3J = 7.2 Hz, 3H, OEt). ^{13}C{^{1}H} NMR (CS_2/C_6D_6, 3:1 v/v %): δ 162.73, 162.64 (*C*O), 144.63, 145.48, 145.46, 145.38, 145.07, 144.96, 144.91, 144.87, 144.82, 144.14, 143.31, 143.25, 142.48, 142.09, 141.19, 141.17, 140.62, 139.56, 139.38, 133.67, 129.24, 129.17 (C_{60}-*C* and Ar-*C*), 71.9 (C_{60}-sp^3), 68.6, (O*C*H_2), 64.2 (*C*H_2N), 63.2 (OEt), 52.2 (C(O)*C*H_2C(O)), 45.6 (N*C*H_3), 14.4 (OEt). MALDI-TOF (9-NA): *m*/*z* 997.0 ([M]$^+$). Anal. Calcd for $C_{75}H_{19}NO_4$: C 90.26, H 1.92, N 1.40. Found: C 90.05, H 1.86, N 1.32.

1,2-Dihydro-61-ethoxycarbonyl-61-{bis{4′-[(dimethylamino)methyl]phenyl}methyloxycarbonyl}-1,2-methano[60]fullerene (15). To a solution of **9** (0.41 g, 0.99 mmol), C_{60} (0.86 g, 1.2 mmol), and I_2 (0.51 g, 2.0 mmol) in toluene (900 mL) was added DBU (0.90 mL, 7.0 mmol) dropwise. The reaction mixture was stirred for 17 h and poured on top of a silica gel column. Elution with toluene afforded 0.23 g of unreacted C_{60}. Elution with toluene/MeOH (95:5 v/v %) gave the crude product after evaporation of the solvent. This was dissolved in CS_2 (10 mL), and acetone was added (75 mL), whereupon the product precipitated. This was isolated, washed with acetone (40 mL), and dried in vacuo, yielding **15** as a light brown solid (0.53 g, 47%, 54% based on reacted C_{60}). ^{1}H NMR ($CDCl_3$): δ 7.41 (d, ^3J = 8.1 Hz, 4H, Ar-*H*), 7.31 (d, ^3J = 8.1 Hz, 4H, Ar-*H*), 7.26 (s, 1H, OC*H*), 4.51 (q, ^3J = 7.5 Hz, 2H, OEt), 3.41 (s, 4H, CH_2N), 2.23 (s, 12H, NCH_3), 1.14 (t, ^3J = 7.2 Hz, 3H, OEt). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 163.51, 162.72 (*C*O), 145.30, 145.26, 145.20, 145.17, 145.15, 145.03, 144.91, 144.91, 144.88, 144.71, 144.69, 144.67, 144.63, 144.46, 143.89, 143.83, 143.06, 143.01, 142.98, 142.97, 142.22, 142.21, 140.94, 142.21, 141.86, 140.94, 140.90, 139.63, 139.36, 138.51, 137.61, 129.16, 127.62 (C_{60}-*C* and Ar-*C*), 79.7 (O*C*H), 71.5 (C_{60}-sp^3), 64.0 (*C*H_2N), 63.5 (OEt), 52.1 (C(O)*C*H_2C(O)), 45.5 (N*C*H_3), 14.2 (OEt). MALDI-TOF (9-NA): *m*/*z* 1131.5 ([M]$^+$). Anal. Calcd for $C_{84}H_{30}N_2O_4$: C 89.19, H 2.67, N 2.48. Found: C 89.28, H 2.57, N 2.50.

1,2-Dihydro-61-ethoxycarbonyl-61-{3′-[chloro(DMSO)-platino]-4′-[(dimethylamino)methyl]benzyloxycarbonyl}-1,2-methano[60]fullerene (16). To a solution of **14** (227 mg, 0.227 mmol) in 1,2-dichlorobenzene (50 mL) was added *cis*-$PtCl_2(DMSO)_2$ (101 mg, 0.239 mmol) and a solution of NaOAc (20 mg, 0.24 mmol) in MeOH (20 mL). The reaction mixture was heated at 65 °C for 17 h and evaporated in vacuo. The crude product was extracted with CS_2 (40 mL), filtered, and evaporated in vacuo. The product was washed with MeOH (2 × 40 mL) and Et_2O (2 × 40 mL) and dried in vacuo, yielding **16** as a brown solid (168 mg, 57%). ^{1}H NMR ($CDCl_3$): δ 8.10 (d, ^3J(Pt−H) = 45.9 Hz, ^4J = 1.2 Hz, 1H, Ar-H_{ortho}), 7.26 (dd,

^3J = 7.5 Hz, ^4J = 1.5 Hz, 1H, Ar-H), 7.09 (d, ^3J = 7.8 Hz, 1H, Ar-H), 4.53 (q, ^3J = 7.2 Hz, 2H, OEt), 4.00 (s, ^3J(Pt−H) = 38.1 Hz, 2H, CH_2N), 3.55 (s, ^3J(Pt−H) = 25.6 Hz, 6H, SCH_3), 2.94 (s, ^3J(Pt−H) = 32.4 Hz, 6H, NCH_3), 1.43 (t, ^3J = 6.9 Hz, 3H, OEt). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 163.51, 163.48 (*C*O), 146.89, 145.41, 145.28, 145.24, 145.20, 145.17, 145.14, 144.85, 144.68, 144.65, 144.57, 144.43, 143.86, 143.84, 143.05, 143.01, 142.96, 142.93, 142.22, 142.19, 141.91, 141.89, 140.91, 140.79, 139.25, 138.91, 136.44, 135.08 (^2J(Pt−C) = 52.3 Hz), 132.16, 130.53, 127.70, 125.78, 121.69 (^3J(Pt−C) = 36.9 Hz), 74.7 (^2J(Pt−C) = 53.8 Hz, *C*H_2N), 71.6 (C_{60}-sp^3), 69.7 (O*C*H_2), 63.4 (OEt), 52.3 (N*C*H_3), 46.8 (^2J(Pt−C) = 60.8 Hz, S*C*H_3), 14.2 (OEt). Anal. Calcd for $C_{77}H_{24}ClNO_5PtS$: C 70.83, H 1.85, N 1.07. Found: C 70.76, H 4.64, N 1.14.

1,2-Dihydro-61-ethoxycarbonyl-61-{*4′*-[(dimethylamino)methyl]-*3′*-[iodo(triphenylposphine)platino]benzyloxycarbonyl}-1,2-methano[60]fullerene (17). To a solution of **14** (173 mg, 0.200 mmol), C_{60} (208 mg, 0.288 mmol), and I_2 (100 mg, 0.388 mmol) in toluene (200 mL) was added DBU (0.12 mL, 0.80 mmol) dropwise. The reaction mixture was stirred for 17 h and poured on top of a silica gel column. A purple-colored fraction was eluted with toluene, affording 0.12 g of unreacted C_{60}. Elution with toluene/MeOH (95:5 v/v %, red-colored fraction) gave the crude product after evaporation of the solvent. This was washed with acetone (40 mL) and dried in vacuo, yielding **17** as a light brown solid (118 mg, 37%, 60% based on reacted C_{60}). ^{1}H NMR ($CDCl_3$): δ 7.78−7.72 (m, 6H, PAr-*H*), 7.42−7.33 (m, 9H, PAr-*H*), 7.08 (d, ^3J = 7.7 Hz, 1H, Ar-*H*), 7.04 (d, ^3J = 8.2 Hz, 1H, Ar-*H*), 6.40 (d, ^3J(Pt−H) = 55.3 Hz, ^4J(P−H) = 3.3 Hz, 1H, Ar-H_{ortho}), 4.78 (s, 2H, O*C*H_2), 4.44 (q, 2H, ^3J = 7.1 Hz), 4.12 (d, ^3J(Pt−H) = 26.1 Hz, ^3J(P−H) = 2.7 Hz, 2H, C*H*$_2$N), 3.17 (d, ^3J(Pt−H) = 24.6 Hz, ^3J(P−H) = 2.7 Hz, 6H, NCH_3), 1.31 (t, ^3J = 7.6 Hz, OEt). ^{13}C-{^{1}H} NMR ($CDCl_3$): δ 163.36, 163.26 (*C*O), 148.08, 145.28, 145.26, 145.23, 145.20, 145.14, 145.13, 144.90, 144.71, 144.69, 144.62, 144.58, 144.55, 143.89, 143.10, 143.06, 143.04, 143.00, 142.24, 20, 141.93, 141.81, 140.98, 140.89, 139.06, 135.32 (d, ^4J(P−C) = 10.4 Hz, PAr-C_{ortho}), 132.18, 130.62 (PAr-C_{para}), 128.02, 127.84 (d, ^3J(P−C) = 11.0 Hz, PAr-C_{meta}), 123.71, 121.97, 74.2 (*C*H_2N), 71.6 (C_{60}-sp^3), 69.0 (O*C*H_2), 63.3 (OEt), 53.2 (N*C*H_3), 14.1 (OEt). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 20.1 (^1J(Pt−P) = 4167 Hz). MALDI-TOF (9-NA): *m*/*z* 1454.0 ([M − I]$^+$). Anal. Calcd for $C_{93}H_{33}INO_4PPt$: C 70.64, H 2.10, N 0.89. Found: C 70.46, H 2.11, N 0.86.

1,2-Dihydro-61-ethoxycarbonyl-61-{bis{*4′*-[(dimethylamino)methyl]-*3′*-[iodo(triphenylposphine)platino]}methyloxycarbonyl}-1,2-methano[60]fullerene (18). To a solution of **15** (346 mg, 0.219 mmol), C_{60} (205 mg, 0.285 mmol), and I_2 (100 mg, 0.388 mmol) in toluene (200 mL) was added DBU (0.12 mL, 0.80 mmol) dropwise. The reaction mixture was stirred for 17 h and poured on top of a silica gel column. A purple-colored fraction was eluted with toluene, affording 116 mg of unreacted C_{60}. Elution with toluene/MeOH (95:5 v/v %, red-colored fraction) gave the crude product after evaporation of the solvent. This was washed with hexanes (40 mL) and dried in vacuo, yielding **18** as a light brown solid (168 mg, 33%, 59% based on reacted C_{60}). ^{1}H NMR ($CDCl_3$): δ 7.64−7.57 (m, 12H, PAr-*H*), 7.26−7.23 (m, 18H, PAr-*H*), 6.77 (d, ^3J = 7.2 Hz, 2H, Ar-*H*), 6.34 (d, ^3J = 7.2 Hz, 2H, Ar-*H*), 6.39 (s, 2H, Ar-H_{ortho}), 5.97 (s, 1H, OC*H*), 4.36 (q, 2H, ^3J = 7.2 Hz, OEt), 4.25/3.90 (AB, *J*(AB) = 13.8 Hz, 4H, CH_2N), 3.27, 3.97 (2 × d, ^3J(P−H) = 2.7 Hz, 12H, NCH_3), 1.23 (t, ^3J = 6.9 Hz, OEt). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 163.27, 161.88 (*C*O), 147.04, 145.35, 145.24, 145.15, 145.11, 144.98, 144.84, 144.75, 144.64, 144.58, 144.55, 144.39, 144.34, 143.86, 143.80, 143.10, 143.09, 143.05, 142.96, 142.91, 142.21, 142.13, 141.88, 144.66, 140.92, 140.69, 139.42, 138.62, 135.95 (d, ^1J(P−C) = 6.2 Hz, PAr-C_{ipso}), 134.96 (d, ^4J(P−C) = 10.4 Hz, PAr-C_{ortho}), 134.62 (^2J(P−C) = 2.0 Hz, Ar-*C*), 132.37, 131.54, 130.36 (PAr-C_{para}), 127.75 (d, ^3J(P−C) = 11.2 Hz, PAr-C_{meta}), 123.34, 121.64, 80.4 (O*C*H), 74.3 (*C*H_2N), 71.5 (C_{60}-sp^3), 63.1 (OEt), 54.3, 51.9 (N*C*H_3), 14.1 (OEt). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 17.5 (^1J(Pt−P) = 4174 Hz). MALDI-TOF (9-NA): *m*/*z* 2170.1 ([M − I]$^+$). Anal. Calcd for $C_{120}H_{58}I_2N_2O_4P_2Pt_2$: C 62.73, H 2.54, N 1.22. Found: C 62.59, H 2.46, N 1.18.

Crystal Structure Determinations. X-ray intensities were measured on a Nonius KappaCCD diffractometer with rotating anode (Mo Kα, λ = 0.71073 Å) at a temperature of 150 K up to a maximal resolution of sin ϑ/λ_{max} = 0.65 Å^{-1}. The structures were solved with automated Patterson methods with the program DIRDIF97[17] and refined with the program SHELXL97[18] against F^2 of all reflections. Non-hydrogen atoms were refined freely with anisotropic displacement parameters; hydrogen atoms were refined as rigid groups. The drawings, structure calculations, and checking for higher symmetry were performed with the program PLATON.[19]

Structure 6: crystallized by diffusion of hexanes into a saturated solution of **6** in CH_2Cl_2. $C_{55}H_{54}Cl_2N_2OP_2Pt_2\cdot CH_2Cl_2$, fw = 1366.95, colorless needle, 0.24 × 0.18 × 0.03 mm^3, monoclinic, $P2_1/c$ (No. 14), a = 12.9136(2) Å, b = 29.0033(4) Å, c = 18.1500(2) Å, β = 129.378(1)°, V = 5254.58(12) Å^3, Z = 4, ρ = 1.728 g cm^{-3}, 39 643 measured reflections, 11 898 unique reflections (R_{int} = 0.073). Absorption correction based on multiple measured reflections (μ = 5.624 mm^{-1}, 0.59−0.99 transmission); 618 refined parameters, 0 restraints. The hydroxy and hydrogen substituents at C10 were refined with a disorder model (pseudo-2-fold rotation). R ($I > 2\sigma(I)$): R1 = 0.0366, wR2 = 0.0870. R (all data): R1 = 0.0476, wR2 = 0.0923. S = 1.014. Minimal and maximal residual electron density between −2.14 and 1.75 e/Å^3.

Structure 10: crystallized by diffusion of Et_2O into a saturated solution of **10** in CH_2Cl_2. $C_{33}H_{35}ClNO_4PPt$, fw = 771.13, colorless needle, 0.54 × 0.15 × 0.09 mm^3, orthorhombic, *Pbcn* (No. 60), a =32.2580(2) Å, b = 9.2442(1) Å, c = 20.8170-(1) Å, V = 6207.62(8) Å^3, Z = 8, ρ = 1.650 g cm^{-3}, 93 074 measured reflections, 7101 unique reflections (R_{int} = 0.068). Analytical absorption correction (μ = 4.696 mm^{-1}, 0.13−0.70 transmission); 373 refined parameters, 0 restraints. R ($I > 2\sigma$-(I)): R1 = 0.0222, wR2 = 0.0533. R (all data): R1 = 0.0271, wR2 = 0.0553. S = 1.046. Minimal and maximal residual electron density between −0.89 and 1.11 e/Å^3.

Structure 13: crystallized by diffusion of Et_2O into a saturated solution of **13** in CH_2Cl_2. $C_{60}H_{60}I_2N_2O_4P_2Pt_2$, fw = 1579.02, yellow needle, 0.18 × 0.06 × 0.03 mm^3, monoclinic, *C*2/*c* (No. 15), a = 30.3152(5) Å, b = 11.1579(2) Å, c = 18.7133-(3) Å, β = 116.5565(7)°, V = 5662.01(17) Å^3, Z = 4, ρ = 1.852 g cm^{-3}, 42 384 measured reflections, 6461 unique reflections (R_{int} = 0.070). Analytical absorption correction (μ = 6.130 mm^{-1}, 0.59−0.85 transmission); 359 refined parameters, 3 restraints. The molecule has an exact, crystallographic C_2 symmetry, leading to rotational disorder at carbon C10. R ($I > 2\sigma(I)$): R1 = 0.0269, wR2 = 0.0524. R (all data): R1 = 0.0374, wR2 = 0.0554. S = 1.042. Minimal and maximal residual electron density between −0.83 and 1.47 e/Å^3.

Acknowledgment. This work was supported by the Council for Chemical Sciences of The Netherlands Organization for Scientific Research (CW-NWO).

Supporting Information Available: Tables of X-ray data for complexes **6**, **10**, and **13**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM010500G

(17) Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; Garcia-Granda, S.; Gould, R. O.; Smits, J. M. M.; Smykalla, C. *The DIRDIF97 program system*, Technical Report of the Crystallography Laboratory; University of Nijmegen: The Netherlands, 1997.

(18) Sheldrick, G. M. *SHELXL-97*, Program for crystal structure refinement; University of Göttingen, Germany, 1997.

(19) Spek, A. L. *PLATON*. A multipurpose crystallographic tool; Utrecht University: The Netherlands, 2000.