

transmetalation may be opposed by internal coordination of the organo group. However, transmetalation of a cyclometalated ligand in similar complexes is possible, as will be shown in a forthcoming paper.^{38b}

Conclusions

The reactions of cyclometalated platinum compounds 1-4 with $\text{Hg}(\text{O}_2\text{CR})_2$ involve an oxidative-addition mechanism and most probably proceed via initial nucleophilic attack of the square-planar Pt atom on the Hg center, resulting in formation of an intermediate with a platinum-to-mercury donor bond. The stability of these intermediates depends on the mutual position of the N-donor atoms. The cis intermediates produce via one-electron transfer stable compounds, with a covalent Pt-Hg bond and in which the Pt center is six-coordinate. Differences in the R skeleton, alkyl vs. aryl cyclometalated ligands, as studied for the cis compounds have no influence on the geometry of the complexes formed. In both cases the Hg atom and the organo groups are mutually cis. The reactions of the cis-diorgano compounds are governed by kinetic factors; the formed Pt-Hg complexes result from migration of the more labile nitrogen ligand. By contrast, the more stable trans intermediate produces via two-electron transfer and simultaneous transfer of two carboxylato groups the corresponding platinum(IV) dicarboxylato complexes and metallic mercury. When the monoorgano Pt compounds $\{[2,6-(\text{Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3]\text{PtX}\}$ are used in which the N-donor atoms are fixed in the trans position, products are obtained for which

structures containing a Pt-to-Hg donor bond have been proposed. This would imply that the terdentate ligand stabilizes, by its rigid skeleton and the trans ligands, a five-coordinate square-pyramidal geometry around Pt^{II} . The possibility of exchange of the carboxylato groups in the Pt-Hg complexes is strongly influenced by their coordination modes. Transfer of cyclometalated nitrogen ligands from platinum to another metal (transmetalation) was not observed during any of the present investigations.

Acknowledgment. We greatly acknowledge Dr. D. M. Grove for his continuous interest and critical reading of the manuscript and Dr. A. J. M. Duisenberg for data collection. Investigations were supported in part by the Netherlands Foundation for Chemical Research (SON), with financial aid from the Netherlands Organization for Pure Research (ZWO) (A.L.S. and A.F.M.J.v.d.P.).

Registry No. 1, 38437-99-9; 2, 38438-00-5; 3, 37667-90-6; 4a, 67507-09-9; 4b, 80484-99; 5a, 77774-87-9; 5b, 77774-86-8; 6a, 80532-09-8; 6b, 80515-21-5; 7a, 77774-88-0; 7b, 77774-85-7; 8b, 80502-38-1; 9b, 80502-39-2; 10a, 80502-40-5; 10b, 80502-41-6; 11, 75878-82-9; 12, 75812-28-1; $\{[2,6-(\text{Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3]\text{Pt}(\text{PPh}_3)\}\text{Br}$, 80502-42-7; *cis*- $[\text{PtCl}_2(\text{SEt}_2)_2]$, 15442-57-6; $(2\text{-Me}_2\text{NC}_6\text{H}_4\text{CH}_2)\text{Li}$ -(TMEDA), 80502-43-8; $\text{Hg}(\text{O}_2\text{CMe})_2$, 1600-27-7; $\text{Hg}(\text{O}_2\text{C-}i\text{-Pr})_2$, 19348-33-5.

Supplementary Material Available: A table of observed and calculated structure factors for $[(2\text{-Me}_2\text{NCH}_2\text{C}_6\text{H}_4)_2(\text{MeCO}_2)\text{PtHg}(\text{O}_2\text{CMe})]$ (26 pages). Ordering information is given on any current masthead page.

Contribution from the Anorganisch Chemisch Laboratorium, J. H. van't Hoff Instituut, University of Amsterdam, 1018 WV Amsterdam, The Netherlands

Synthesis of Novel Dinuclear Formamidino and Triazenido Compounds $\{[2,6-(\text{Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3](p\text{-tolNYNR})\text{PtAgBr}\}$ (Y = CH, N) Containing a Platinum-Silver Bond

ANTONIUS F. M. J. VAN DER PLOEG, GERARD VAN KOTEN,* and KEES VRIEZE

Received July 15, 1981

Complexes $\{[2,6-(\text{Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3](p\text{-tolNYNR})\text{PtAgBr}\}$ (Y = CH, N, R = Me, Et, *i*-Pr; Y = CH, R = *p*-tolyl (*p*-tol)) are formed by the reaction of $\{[2,6-(\text{Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3]\text{PtBr}\}$ with $[\text{Ag}(p\text{-tolNYNR})]_n$. In contrast, $\{[2,6-(\text{Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3]\text{PtBr}\}$ and $[\text{Ag}(\text{O}_2\text{CR})]_n$ (R = Me, *i*-Pr) undergo ligand metathesis, resulting in formation of the products $\{[2,6-(\text{Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3]\text{Pt}(\text{O}_2\text{CR})\}$ and AgBr. The proposed structure for the platinum-silver compounds comprises a five-membered chelate ring in which a Pt^{II} -to- Ag^{I} donor bond is bridged by a triazenido (Y = N) or formamidino (Y = CH) group, while the bromide atom, having migrated from the Pt^{II} center, is on the Ag^{I} atom. The bridging bonding mode is inferred from the observation of both $J(^{195}\text{Pt}-^1\text{H})$ (± 38 Hz) and $J(^{107,109}\text{Ag}-^1\text{H})$ (± 16 Hz) for the central H atom of the N-C(H)-N skeleton in the formamidino compounds. Except for *p*-tolNC(H)N-*p*-tol, the compounds exist in two isomers, the relative ratio of which is discussed in terms of steric and electronic factors of the alkyl groups (R), which influence the course of the intimate formation mechanism. Furthermore, it is suggested that the basicity of the Pt center, which has effectively been enhanced by the mutually trans N-donor atoms, contributes to the stability of the Pt-Ag donor bond.

Introduction

In previous reports it has been shown that square-planar d^8 -electron species such as $[\text{L}_2(\text{CO})\text{MX}]$ (L = Ph_3P , Ph_3As , PhMe_2P ; M = Rh, Ir; X = Cl, Br, I) can form stable covalently bonded dinuclear complexes with Hg^{II} salts¹⁻⁴ and stable M-to-M' donor-bonded complexes with Cu^{I} and Ag^{I} com-

pounds.⁵⁻⁸ The formation of these complexes can be ascribed to the basic character of the group 8B metal center in $[\text{L}_2(\text{CO})\text{MX}]$, and the presence of bridging ligands such as nitrate,⁷ perchlorate,⁷ carboxylato,^{2,7,9} amidino, and triazenido^{2,3,8} groups determines to a large extent the stability of these dinuclear complexes.

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Table I. Analytical Data and Characteristic Infrared Absorptions

compd	anal. found (calcd)				IR, 1600–1100-cm ⁻¹ region ^a
	% C	% H	% N	other	
{[2,6-(Me ₂ NCH ₂) ₂ C ₆ H ₃][p-tolNC(H)NMe]PtAgBr}	35.39 (34.97)	4.15 (4.16)	7.75 (7.76)		1588, 1339, 1230
{[2,6-(Me ₂ NCH ₂) ₂ C ₆ H ₃][p-tolNC(H)NEt]PtAgBr}	36.13 (35.94)	4.45 (4.35)	7.59 (7.62)		1580, 1335, 1260, 1225
{[2,6-(Me ₂ NCH ₂) ₂ C ₆ H ₃][p-tolNC(H)N- <i>i</i> -Pr]PtAgBr}	36.77 (36.85)	4.58 (4.54)	7.33 (7.47)	11.19 ^b (10.68)	1575, 1342, 1265, 1231
{[2,6-(Me ₂ NCH ₂) ₂ C ₆ H ₃][p-tolNC(H)N- <i>p</i> -tol]PtAgBr}	40.93 (40.76)	4.46 (4.62)	6.90 (7.02)		1555, 1343, 1222
{[2,6-(Me ₂ NCH ₂) ₂ C ₆ H ₃](p-tolNNMe)PtAgBr}	33.32 (33.25)	4.08 (4.05)	9.56 (9.69)		1460, 1423, 1362, 1310, 1275
{[2,6-(Me ₂ NCH ₂) ₂ C ₆ H ₃](p-tolNNNEt)PtAgBr}	33.43 (33.50)	4.14 (4.17)	9.15 (9.15)		1425, 1408, 1255
{[2,6-(Me ₂ NCH ₂) ₂ C ₆ H ₃](p-tolNNN- <i>i</i> -Pr)PtAgBr}	35.15 (35.21)	4.45 (4.43)	9.23 (9.33)		1458, 1388, 1250
{[2,6-(Me ₂ NCH ₂) ₂ C ₆ H ₃][Pt(O ₂ CMe)]·H ₂ O}	36.74 (36.28)	4.85 (5.22)		10.17 ^c (10.36)	1578, 1410
{[2,6-(Me ₂ NCH ₂) ₂ C ₆ H ₃][Pt(O ₂ C- <i>i</i> -Pr)]}	40.20 (40.58)	5.41 (5.50)		7.78 ^c (6.76)	1595, 1390

^a Only bands associated with formamido, triazeno, and carboxylato moieties. ^b % Br. ^c % O.

Recently, it has been demonstrated by ourselves¹⁰ and others¹¹ that organoplatinum(II) compounds containing nitrogen-donor ligands can form Pt–Hg-bonded complexes with mercury(II) carboxylates. Whereas normally Pt^{II} is a softer base than Rh^I and Ir^I, the enhanced electron-donating ability of this type of Pt^{II} center is very likely due to the presence of the nitrogen-donor ligands rather than of tertiary phosphines. This prompted us to investigate whether this donating ability is pronounced enough to also form M-to-M' donor-bonded complexes with metal centers other than Hg^{II}.

In this paper we report reactions of the platinum(II) compound {[2,6-(Me₂NCH₂)₂C₆H₃]PtBr}₂,¹² which has two mutually trans N-donor ligands, with silver(I) carboxylato, formamido, and triazeno compounds. The influence of the bulk of alkyl substituents R in the *p*-tolNYNR ligands on the formation of possible isomeric compounds is also discussed.

Experimental Section

¹H NMR spectra were recorded on Varian T60 and Bruker WM250 spectrometers. The IR spectra were measured on a Perkin-Elmer 283 instrument. Elemental analyses were carried out at the Institute for Organic Chemistry TNO, Utrecht, The Netherlands. The syntheses of {[2,6-(Me₂NCH₂)₂C₆H₃]PtBr}₂¹² and polynuclear [Ag(RNYNR')]_n (Y = N, CH)¹³ are described in the literature.

Synthesis of {[2,6-(Me₂NCH₂)₂C₆H₃]Pt(O₂CR)} (R = Me, *i*-Pr). Silver carboxylate, Ag(O₂CR) (0.2 mmol), was added to a solution of {[2,6-(Me₂NCH₂)₂C₆H₃]PtBr} (0.093 g, 0.2 mmol) in CH₂Cl₂ (5 mL) and the mixture stirred overnight. The resulting gray precipitate of AgBr was filtered off and the filtrate concentrated to 2 mL by evaporation of the solvent in vacuo. Addition of pentane (5 mL) gave a white precipitate of pure {[2,6-(Me₂NCH₂)₂C₆H₃]Pt(O₂CR)}, which was filtered off, washed with pentane, and dried in vacuo. Recrystallization from CH₂Cl₂–pentane in air gave the acetato compound (R = Me) containing 1 mol of H₂O. The yield was 90% for both compounds.

Synthesis of {[2,6-(Me₂NCH₂)₂C₆H₃]p-tolNC(H)NR}PtAgBr (R = Me, Et, *i*-Pr, *p*-tol). Silver formamidine [Ag{p-tolNC(H)NR}]_n (1/5*n* mmol) was added to a solution of {[2,6-(Me₂NCH₂)₂C₆H₃]PtBr} (0.093 g, 0.2 mmol) in CH₂Cl₂ (5 mL) and stirred overnight. The

Table II. ¹H and ¹³C NMR Data for {[2,6-(Me₂NCH₂)₂C₆H₃]Pt(O₂CR)}^a

	¹ H NMR				
	aryl H	NCH ₂	NCH ₃	carboxylate	
				C _α H	C _β H
R = Me	6.80	3.98 (50)	3.02 (38)	2.06	
R = <i>i</i> -Pr	6.90	4.05 (50)	3.05 (38)	2.62	1.23

	¹³ C NMR							
	aryl			carboxylate				
	C(2)	C(3)	C(4)	NCH ₂	NCH ₃	CO ₂	C _α	C _β
R = Me	143.7	119.1	122.9	76.9	53.3		25.2	
		(35)			(18)		(15)	
R = <i>i</i> -Pr	143.6	118.9	122.8	76.9	53.1	183.2	37.3	20.3
		(34)			(19)		(18)	

^a In CDCl₃, δ (X) relative to Me₄Si, J(¹⁹⁵Pt–X) in parentheses (X = ¹H, ¹³C).

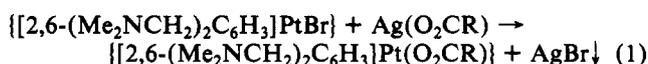
somewhat turbid solution was filtered and concentrated to 2 mL. Addition of pentane (10 mL), stirring of the mixture, and filtration gave {[2,6-(Me₂NCH₂)₂C₆H₃][p-tolNC(H)NR]PtAgBr} as a white amorphous residue. This was washed with pentane and dried in vacuo; yield 90%.

Synthesis of {[2,6-(Me₂NCH₂)₂C₆H₃](p-tolNNNR)PtAgBr} (R = Me, Et, *i*-Pr). A solution of silver triazene, [Ag(p-tolNNNR)]_n (1/5*n* mmol), and {[2,6-(Me₂NCH₂)₂C₆H₃]PtBr} (0.093 g, 0.2 mmol) in CH₂Cl₂ (5 mL) was stirred 18 h. The originally yellow solution, which had become colorless and slightly turbid, was filtered and concentrated to 2 mL. Addition of pentane (10 mL) gave a white precipitate of pure {[2,6-(Me₂NCH₂)₂C₆H₃](p-tolNNNR)PtAgBr}, which was filtered off, washed with pentane, and dried in vacuo; yield 80%.

Attempted Reaction of {[2,6-(Me₂NCH₂)₂C₆H₃]PtBr} with [Ag(p-tolNNN-*p*-tol)]_n. Silver triazene, [Ag(p-tolNNN-*p*-tol)]_n (0.066 g, 1/5*n* mmol), was added to a solution of {[2,6-(Me₂NCH₂)₂C₆H₃]PtBr} (0.093 g, 0.2 mmol) in CH₂Cl₂ (10 mL) and was stirred overnight. The yellow suspension was filtered off, leaving unreacted [Ag(p-tolNNN-*p*-tol)]_n as the residue. Evaporation of the solvent from the filtrate resulted in the recovery of {[2,6-(Me₂NCH₂)₂C₆H₃]PtBr}.

Results

Reaction of the organoplatinum(II) compound {[2,6-(Me₂NCH₂)₂C₆H₃]PtBr} with silver carboxylates resulted in elimination of AgBr and formation of organoplatinum carboxylato compounds according to eq 1.



R = Me, *i*-Pr

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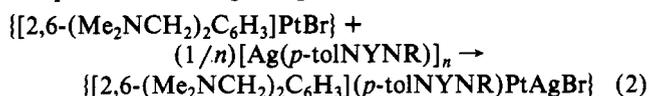
Table III. ^1H NMR Data for $\{[2,6-(\text{Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3](p\text{-tolNYNR})\text{PtAgBr}\}^a$

Y	R	isomer ^b	[2,6-(Me ₂ NCH ₂) ₂ C ₆ H ₃] resonances						p-tolNYNR resonances					
			aryl		CHH ^c	N(Me)Me ^d		CH	p-tolyl			alkyl		
			m-H ^e	p-H ^e		o-H	m-H		CH ₃	C _α	C _β			
CH	Me	A	7.08	6.94	4.54	4.04	3.07	2.76 (40)	8.69 (-, 17)	7.57	7.08	2.28	3.22 (-, 4)	
		B	7.08	6.94	4.55 (45)	4.05 (57)	3.17 (43)	2.98 (38)	8.84 (46, 16)	7.10 (s)		2.26	3.37 (14, -)	
CH	Et	A	7.05	6.91	4.51 (48)	4.00 (54)	3.06 (44)	2.76 (39)	8.67 (38, 16)	7.48	7.08	2.28	3.43 (-, 6)	
		B			4.52	4.00	3.15 (43)	2.94 (38)	8.76	7.02 (s)		2.27	3.63	
CH	i-Pr	A	7.05	6.91	4.50 (47)	3.99 (55)	3.06 (43)	2.74 (37)	8.76 (38, 16)	7.49	7.07	2.27	3.57 (-, 10)	
		B											1.44	
CH	p-tol	A	7.09	6.94	4.56 (49)	4.04 (51)	3.05 (42)	2.74 (37)	8.89 (39, 14)	7.54	7.16	2.28		
		B								7.11 (s)		2.26		
N	Me	A					3.04	2.80 (38)	8.04	7.11		3.68		
		B	7.07	6.92	4.49 (46)	4.03 (56)	3.13 (41)	2.97 (38)	7.41	7.06	2.29	3.82		
N	Et	A	7.09	6.92	4.48	4.02	3.13	2.79 (37)	8.04	7.10	2.30	3.83		
		B			4.50	4.04	3.13 (43)	2.94	7.42	7.10	2.28	3.84		
N	i-Pr	A	7.09	6.92	4.49 (48)	4.03 (54)	3.04 (44)	2.79 (38)	8.04	7.10	2.30	4.05		
		B							7.41			1.51		

^a In CD₂Cl₂; ¹H is in ppm relative to Me₄Si, $J(^{195}\text{Pt}-^1\text{H})$, followed by $J(^{107,109}\text{Ag}-^1\text{H})$ where appropriate, in parentheses. ^b A = alkyl N atom bonded to Ag; B = alkyl N atom bonded to Pt. ^c Doublets with $J(\text{H}-\text{H})_{\text{gem}} = 13$ Hz. ^d Singlets. ^e Multiplets.

The acetato compound was obtained as the water adduct. The platinum compounds have been identified by elemental analyses and IR spectroscopy (Table I) and ^1H and ^{13}C NMR (Table II). The trans(N) configuration and inert Pt-N coordination have been retained, as deduced from the observation of platinum couplings with the CH₂NMe₂ H and C atoms (Table II). Coordination of the carboxylato group to platinum is indicated by $J(^{195}\text{Pt}-^{13}\text{C})$ for C_α (15 Hz, R = Me; 18 Hz, R = *i*-Pr), and a monodentate bonding mode is inferred from the difference of 170 cm⁻¹ between $\nu(\text{CO}_2)_{\text{asym}}$ and $\nu(\text{CO}_2)_{\text{sym}}$ (Table I). Thus a square-planar geometry around platinum will be valid for these platinum(II) carboxylates.

Reaction of the platinum compound $\{[2,6-(\text{Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3]\text{PtBr}\}$ with silver formamido and triazenido compounds resulted in formation of platinum-silver compounds according to eq 2.



Y = CH, N, R = Me, Et, *i*-Pr; Y = CH, R = *p*-tol

The platinum-silver complexes are readily soluble in CH₂Cl₂ but only slightly soluble in benzene or toluene. They are also soluble in CHCl₃ but decompose within 0.5 h, resulting in elimination of AgX and, according to ^1H NMR, quantitative formation of *p*-tolNYN(H)R and $\{[2,6-(\text{Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3]\text{PtX}\}$ (X = Cl, Br). It seems likely that this decomposition is due to the ease with which CHCl₃ eliminates H and Cl and generates CCl₂ carbenes.

Elemental analyses of the platinum-silver complexes pointed to the stoichiometries indicated in Table I. The IR spectra of these complexes showed strong absorptions, in the region of 1000–1600 cm⁻¹ (Table I), which are probably due to the N–Y–N skeleton but certainly not to the terdentate ligand [2,6-(Me₂NCH₂)₂C₆H₃], the characteristic absorptions of that ligand being known from $\{[2,6-(\text{Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3]\text{PtBr}\}$.

Surprisingly, the values we find for the triazenido compounds do not meet the criteria deduced by others for the respective bonding modes: monodentate, chelate and bridging.^{6,14,15} However, it is very well possible that those criteria are only valid for bis(aryl)-substituted triazenido compounds, since the absorptions for the present platinum-silver compound $\{[2,6-(\text{Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3](p\text{-tolNNNMe})\text{PtAgBr}\}$ (1362, 1310,

Table IV. Relative Abundance of the Isomers of $\{[2,6-(\text{Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3](p\text{-tolNYNR})\text{PtAgBr}\}^a$

Y	R	isomer A ^b	isomer B ^c	ln ([A]/[B])
CH	Me	29	71	-0.90
CH	Et	83	17	1.59
CH	<i>i</i> -Pr	99	1	4.60
N	Me	19	81	-1.45
N	Et	67	33	0.71
N	<i>i</i> -Pr	98	2	3.89

^a Based on the intensities of the ^1H NMR resonances. ^b Alkyl N atom bonded to Ag. ^c Alkyl N atom bonded to Pt.

and 1275 cm⁻¹) are very similar to those reported for the heterodinuclear compound $[(\text{Ph}_3\text{P})_2(\text{CO})(p\text{-tolNNNMe})\text{RhCuCl}]$ (1369, 1319, and 1278 cm⁻¹), for which a structure with a Rh-to-Cu bond bridged by one ligand has been proposed.^{5,16a} Unfortunately, we have not been able to synthesize the [bis(*p*-tolyl)triazenido]platinum-silver compound to clarify the situation above.

From the ^1H NMR spectra (Table III) it is clear that in solution each compound, except for *p*-tolNC(H)N-*p*-tol, exists in two isomeric forms, whose ratio depends on whether the alkyl group is Me, Et, or *i*-Pr (Table IV; vide infra). The abundance of some of the isomers was too low for a complete assignment of all the NMR resonances, since they overlapped with resonances of the other isomer. As far as assignments are possible, they indicate that the compounds are isostructural.

For the formamido compounds the resonance pattern for the central hydrogen atom N–C(H)–N gives very convincing evidence for the bridging mode of this ligand. This H atom couples with both silver and platinum as has been deduced from the observation of a doublet flanked by doublet satellites. The doublet splitting is due to coupling with silver.¹⁷ It must be noted that the doublets due to coupling with the isotopes ¹⁰⁷Ag (52%; $I = 1/2$) and ¹⁰⁹Ag (48%; $I = 1/2$), respectively, are not separated but coincide. This results from the small ratio of their gyromagnetic constants (1.14) in combination with a small J value (mean 16 Hz). The satellites, which have a 1:4 intensity ratio with respect to the central doublet, arise from coupling with ¹⁹⁵Pt ($I = 1/2$, 33%; $J = 34$ Hz). Although very few examples have been reported for couplings between Ag and H atoms (e.g., $^3J(^{107,109}\text{Ag}-\text{N}=\text{C}-^1\text{H}) = 6.3$ and

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(17) This has been established by ¹⁰⁹Ag coupling experiments and by ¹⁰⁹Ag INEPT NMR spectroscopy.²⁵

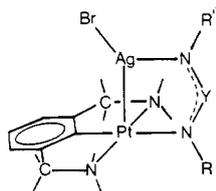


Figure 1. Proposed structure for the compounds $\{[2,6-(\text{Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3](\text{R}'\text{NYNR}')\text{PtAgBr}\}$: isomer A, R = *p*-tolyl, R' = alkyl; isomer B, R = alkyl, R' = *p*-tolyl.

9.3 Hz for two different sites, respectively, in $\{\text{Ag}_2[\mu-(R,S)-1,2-[(2-\text{C}_5\text{H}_4\text{N})\text{C}(\text{H})=\text{N}]_2\text{-cyclohexane}]_2[\text{O}_3\text{SCF}_3]_2\}^{18a}$ and $^3J(^{107,109}\text{Ag}-\text{C}=\text{C}-^1\text{H}) = 7.2$ Hz in $[\text{Ag}_2\text{Li}_2(\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2)_4]^{18b}$, we have confidence in the above assignment, since none of the other nuclei present in the formamidino ligand are likely to be responsible for that coupling.

With the above considerations in mind, the observation of two isomers for each compound $\{[2,6-(\text{Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3][p\text{-tolNC}(\text{H})\text{NR}]\text{PtAgBr}\}$ in which R = alkyl can be expected to result from different orientations of the unsymmetric bridging *p*-tolNC(H)NR ligand (see Figure 1); i.e., *p*-tol-N can either be bonded to Pt and alkyl-N to Ag (isomer A) or the other way around (isomer B). As a consequence, for R = *p*-tol only one isomer is to be expected.

The isomers (A and B) could be assigned on the following basis. In the resonance patterns of one of the two isomers of the formamidino-bridged compounds the multiplet for the C_αH atoms of the alkyl group is split into a doublet pattern as a result of coupling with another nucleus ($J = 4$ Hz, R = Me; $J = 6$ Hz, R = Et; $J = 10$ Hz, R = *i*-Pr). This observation can only be attributed to coupling with silver, as was likewise observed for the central H atom. Therefore, it is assumed that this alkyl-N group is the one bonded to Ag (isomer A). It is then found that the alkyl groups in these isomers (A) are always shifted upfield with respect to the alkyl-N groups, which are bonded to Pt in the other isomers (B). Only for the A isomers, containing the alkyl-N group bonded to Ag and thus the *p*-tol-N bonded to Pt, do the *p*-tol H atoms appear as an AB pattern in the ^1H NMR spectrum (δ 7.54 and 7.11, $J(\text{H}-\text{H}) = 14$ Hz). For the *p*-tolyl group of the other isomer the H atoms appear as a singlet (δ 7.11). For the *p*-tolNC(H)N-*p*-tol compound both an AB pattern and a singlet were observed, which is in accordance with a structure in which one *p*-tol-N is bonded to Pt and the other to Ag. For the methyl H atoms of the two *p*-tolyl groups two resonances are observed, differing by 0.02 ppm in chemical shift, in accordance with the formamidino ligand bridging two unlike metal centers.

In the ^1H NMR spectra of all the formamidino compounds two singlets are observed for the NMe_2 groups, with inequivalent $J(^{195}\text{Pt}-^1\text{H})$ couplings, and for the CH_2 atoms an AB pattern also with $J(^{195}\text{Pt}-^1\text{H})$ couplings. The observation of these couplings indicate the occurrence of inert Pt-N coordination as discussed for the structural elucidation of $[2-[(\text{dimethylamino})\text{methyl}]\text{phenyl}]\text{platinum-mercury acetate}$ complexes in solution.^{10b} The respective chemical shifts and platinum coupling constants for the CH_2NMe_2 H atoms in the two isomers do not differ very much. The values at slightly higher fields have been obtained for the isomer with the *p*-tol N atom bonded to Pt (Figure 1, isomer A). The platinum coupling constants ($\text{CH}_2 \pm 50$ Hz, $\text{NMe} \pm 40$ Hz) are in accordance with other planar-coordinated platinum(II) compounds in which the N atoms are mutually trans bonded (e.g.,

CH_2 42 Hz, NMe 45 Hz in *trans*- $[(2-\text{Me}_2\text{NCH}_2\text{C}_6\text{H}_4)_2\text{Pt}]^{19}$).

From the CH_2NMe_2 H resonances one may conclude that the two NMe_2 groups and the two CH_2 groups are enantiotopic, indicating a mirror plane through Pt and the central axis of the terdentate ligand, and perpendicular to that ligand. Furthermore, the CH_2 H atoms and the NMe_2 Me groups have become diastereotopic, as indicated by their chemical shift and coupling inequivalence, which means that the C and N atoms, respectively, are not C_2 centers, and thus a mirror plane containing the aryl-N₂ ligand is absent. These facts can be explained with a structure in which the planes through the bridging ligand and the aryl-N₂ ligand are mutually perpendicular.

For the triazenido compounds deduction of the bridging bonding mode of the triazenido ligand from couplings with Ag and Pt on a central H atom as in the formamidino compounds is not possible. Furthermore, no coupling has been observed between Ag and the α -H atoms of any of the triazenido alkyl groups. This does not exclude a coordination between the alkyl-N and Ag but indicates that such a coordination, if present, is somewhat less rigid than in the formamidino compounds (see Discussion).

For the triazenido compounds two isomers are also present, the molar ratio of which changed with the bulkiness of the alkyl substituent (Table IV), thus allowing the assignments shown in Table III. Furthermore, the similarities between their spectral data and those of the formamidino compounds (Table III) suggest that the compounds are isostructural.

From several crystal structures it has appeared that coordinated formamidino and triazenido groups M-N-Y-N- are normally present in a cis conformation that, moreover, is (almost) planar. A similar cis conformation for both Pt-N-Y-N' and N-Y-N'-Ag moieties is very likely for the present Pt-Ag complexes, since it allows interaction between the two metal atoms, probably involving the electrons in the d_{z^2} orbital on Pt (vide infra). In this conformation the *p*-tolyl and R substituents on the N-Y-N' fragment have minimal steric interaction whereas in the alternate trans conformation for Pt-N-Y-N' and N-Y-N'-Ag, the organo substituents are positioned such that they experience large steric hindrance with the other cis substituent.

These results relating to the coordination of the terdentate ligand and of the bridging group in combination with the symmetry requirements derived from the NMR data suggest that the Br atom has migrated to the silver center, and the most probable structure on this evidence is illustrated in Figure 1. Thus, the structure of the present Pt-Ag complexes consists of a square-pyramidal-surrounded Pt center with an apical-positioned silver atom, which is bonded to the migrated bromide atom. The Pt-Ag unit is bridged by the *p*-tolNYNR ligand.

Similar structural features have been observed for $\{[2,6-(\text{Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3](p\text{-tolNYNR})\text{PtHgX}_2\}$, and the proposed structure, containing a Pt-to-Hg donor bond, has been established for R = *i*-Pr, $\text{X}_2 = \text{ClBr}$, and Y = CH.²⁵

Discussion

Stability of Platinum–Silver Complexes. Complexes $\{[2,6-(\text{Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3](p\text{-tolNYNR})\text{PtAgBr}\}$ (Y = CH, N, R = Me, Et, *i*-Pr; Y = CH, R = *p*-tol) are the first examples of stable heterodinuclear compounds in which Pt and Ag are bridged by a R'NYNR' ligand. Attempts to prepare similar complexes with the isostructural and isoelectronic carboxylato group failed. The deduced conformation of these complexes (see Figure 1), which could be established for an analogous Pt-Hg formamidino compound²⁵ (see Results), is stable on

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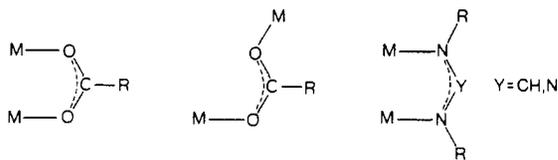


Figure 2. Schematic representation for syn and gauche bridge bonding modes for carboxylato and formamidino (triazenido) ligands (see text).

the NMR time scale, and this is reflected in particular by the fact that, in the case of the formamidino complexes, platinum and silver couplings on the NC(H)N unit could be observed. Reports of $J(^{107,109}\text{Ag}-\text{H})$ are not very common and seem only to deal with those cases where compounds have inert ligand-metal coordination on the NMR time scale.^{17,18}

Our new complexes are a logical extension of the Ir-(Rh)-Ag(Cu) compounds $[\text{L}_2(\text{CO})(\text{L}-\text{L})\text{MM}'\text{X}]$ (L = PPh_3 ; L-L = RCO_2 , X = RCO_2 ; L-L = $\text{RNC}(\text{H})\text{NR}'$, RNNNR' , X = Cl, Br)⁵⁻⁸ in which monoanionic RNYNR' or RCO_2 ligands bridge a d^8-d^{10} metal combination. Notable examples of such structures confirmed by X-ray structure determinations are $[(\text{PPh}_3)_2(\text{CO})(p\text{-tolN}(\text{N}(\text{N})\text{Me})\text{IrAg}(\text{O}_2\text{C}-i\text{-Pr})(\text{HO}_2\text{C}-i\text{-Pr})]$ (Ir-Ag 2.874 (2) Å)^{16b} and $[(\text{PPh}_3)_2(\text{CO})(\text{MeNN}(\text{N}-\text{Me})\text{RhCuCl}]$ (Rh-Cu 2.73 Å),^{16a} the latter being also an example in which the halogen atom has migrated from the d^8 metal (Rh) to the d^{10} metal (Cu). The bonding in these complexes has been described in terms of a direct Ir(Rh)-to-Cu(Ag) donor bond, accomplished by interaction of the metal d_z orbital with an empty orbital combination on the group 1B metal atom. As a consequence this latter metal center in these complexes has a three-coordinate geometry, which is commonly found in group 1B metal chemistry. The basicity of the donor metal atom in these d^8-d^{10} metal combinations is of importance.

In view of the decreasing basicity in the series Ir > Rh >> Pt it is not surprising that until now compounds with stable Pt-Cu(Ag) donor bonds have not been isolated. However, the present complexes show that if the inherent Pt^{II} basicity is effectively enhanced, the stability of such bonds can be considerable. From other work involving the use of the terdentate $(\text{Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3$ ligand it was concluded that for this purpose this ligand system would be particularly suited.¹⁰ Its geometry fixes the hard donor ligands in mutually trans orientations in the ligand sphere of the metal. A second factor that may add to the stability of the final Pt-Ag complexes is the planar configuration of this terdentate ligand system, coincident with the Pt coordination plane, which will necessarily reduce destabilizing steric interactions with coligands above and below this plane.

Another stabilizing factor is the presence of the bridging $p\text{-tolN}(\text{N}(\text{N})\text{R})$ ligand, which coordinates via hard donor atoms to both Pt and Ag and completes a five-membered ring system in which electron delocalization possibly occurs.

Formation of the complexes must have involved migration of the halide atom, a process that has also been observed to occur in other reactions leading to heterodinuclear complexes.^{2-8,10,25} Transfer of a halide is usually part of exchange reactions with silver carboxylates^{20,21} and has been observed in this work for the reaction of $\{[2,6-(\text{Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3]\text{PtBr}\}$ with $\text{Ag}(\text{O}_2\text{CR})$. It seems plausible that in the latter reaction a heterodinuclear Pt-Ag complex is formed that is isostructural to the formamidino and triazenido complexes. Apparently, these carboxylato-bridged complexes have low stability, thereby pointing to the importance of the nature of the bridging ligands.

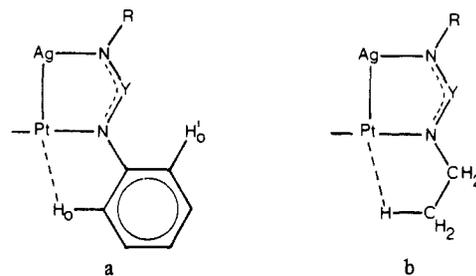


Figure 3. Schematic representation for the geometries with (a) p -tolyl and (b) alkyl groups, respectively, near the vacant site at platinum in $\{[2,6-(\text{Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3](p\text{-tolN}(\text{N}(\text{N})\text{R})\text{PtAgBr})$.

The nature of the stabilizing effect of the triazenido or formamidino ligands on the M-to-M' interaction compared to that of the carboxylates may be the following. The oxygen atoms in the carboxylate groups have two lone pairs each, which can coordinate either in the syn or gauche bridge bonding modes for those ligands (see Figure 2). Very likely these modes can be interconverted when the bridged metals are not bonded to each other. For the triazenido and formamidino ligands only one bridging bonding mode is possible (syn), which, very likely, results in much more rigid structures.

It is noteworthy that $\text{Ag}(\text{O}_2\text{CR})$ with $[\text{Me}_2\text{Pt}(\text{SR}_2)]_2$ dimer gave a redox reaction resulting in Ag^0 and the Pt-Pt-bonded compound $[\text{Me}_4\text{Pt}_2(\text{SR}_2)_2(\text{O}_2\text{CR})_2]$.²² It may be questioned whether these reactions have proceeded via carboxylato-bridged Pt-Ag compounds with structures analogous to those presently observed. Migration of a halogen from Pt to Ag, which has been seen to be an essential step for the formation of stable bridged Pt-Ag complexes, is not possible with the dimeric $[\text{Me}_2\text{Pt}(\text{SR}_2)]_2$ compounds. Further study is required to elucidate the mechanism of this redox reaction.

Deshielding. Different chemical shifts have been observed for the alkyl and aryl groups bonded either to N(Pt) or to N(Ag). The deshielding of the ortho H atoms of the N-(Pt)-bonded p -tolyl group (Figure 1, isomer A) can be explained with a geometry in which the ortho H atoms reside near a vacant site at platinum, i.e., when the p -tolyl group is positioned under the Pt atom (Figure 3a). In this position these H atoms experience the anisotropy of the Pt atom (rotation around the N-C(p -tol) axis brings both H atoms alternately near the Pt center). Deshielding of the β -methyl H atoms in the N(Pt)-bonded alkyl groups (isomer B) compared with those of the N(Ag)-bonded groups can be explained with a similar geometry (Figure 3b) and reasoning.

It is interesting to note that nonbonding intramolecular M-H interactions have been reported for several square-planar d^8 complexes, and downfield shifts of about 2 ppm for such H atoms are not uncommon.²³ For the respective H atoms in the present complexes the downfield shifts are relatively small. This might be due to the fact that the H atoms of the R groups are not fixed near the Pt center; NMR spectra are fully consistent with rotation of the R group. A second reason might be the fact that the electron density in the d_z orbital at platinum, which is mainly responsible for the magnetic anisotropy, is already shifted toward the Pt-to-Ag donor bond.

Influence of the Alkyl Substituent on the Isomer Ratio. For the Pt-Ag compounds bridged by a $p\text{-tolN}(\text{N}(\text{N})\text{alkyl})$ ligand two isomers are possible that have the alkyl N atom bonded either to Ag (Figure 1, isomer A) or to Pt (isomer B) (vide supra). An interesting point is the fact that the isomer ratio seems to be dependent on the type of alkyl substituent (Table

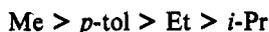
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IV). Though the absolute values of the ratios must be handled with precaution, since for certain complexes the overall yields were not quantitative and for others low abundance of one of the two isomers hindered accurate measurements, the results in Table IV nevertheless indicate a trend. It is clear that the ratio [A]/[B] gradually increases in going from R = Me via Et to *i*-Pr and for the formamidino compounds it is always higher than that for the corresponding triazenido compounds. The preference for the alkyl substituent to be N(platinum) bonded is

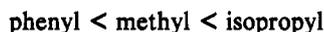


The observed order can be the result of (i) the formation mechanism (kinetic determination) or of (ii) the relative thermodynamic stability of the isomers (thermodynamic determination).

Van Vliet et al. suggested a mechanism for the formation of bridged Ir–Cu(Ag) complexes $[(\text{Ph}_3\text{P})_2(\text{CO})\text{IrM}(p\text{-tolN}(\text{YNR})\text{Cl})]$ (M = Ag, Cu) in which breakdown of the polynuclear complex $[\text{M}(p\text{-tolN}(\text{YNR}))_n]$ resulted in formation of a Ir–M-bonded intermediate with the *p*-tolN(YNR) group still on M.⁸ In fact, in that stage the *p*-tolN(YNR) group can be bonded either as a chelating ligand or as a monodentate ligand that can exchange its bonding site. Formation of the bridging bonding mode then requires breaking of one M–N bond, correct positioning of that N atom in the neighborhood of the free coordination side at the transition metal, and bond making between that N atom and the transition metal.

The stability of the metal–N bonds and thus also metal–N bond breaking and bond making will be influenced by the relative basicity of the ligand halves and the basicity of the complete ligand and of the metal centers. The difference in basicity of the formamidino and triazenido ligands may thus be responsible for the systematically higher isomer ratio in the case of the present Pt–Ag formamidino complexes (Table IV). The relative basicity of the ligand halves will depend on the substituent and in fact will increase in the order Me < Et < *i*-Pr.

The required orientation of the *p*-tolN(YNR) group relative to the other ligands on the transition metal may introduce steric requirements. In this respect it is interesting to note that Brunner et al.²⁴ obtained the order for the steric hindrance of R on the rotation of the aryl group in $\{(\text{Cp})(\text{CO})_2\text{Mo}[\text{SC}(\text{aryl})\text{NR}]\}$

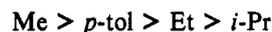


They suggested that the small steric hindrance of the phenyl group is caused by the fact that it can turn away from the aryl group.

Interestingly, the thermodynamic stability will also be determined by electronic and steric factors, and these will both demand the same preference, with the smallest and less basic NR grouping bonded to platinum, because platinum is already coordinated by two NMe₂ donor groups, while the more acidic silver center will be coordinated by the more basic ligand side. However, the existence of an equilibrium between the isomers could not be observed. Consequently, the observed ratio is a

clear reflection of the factors that play a role during complex formation (cf. discussion in ref 25).

It is also interesting to note that for the compounds $[(\text{Ph}_3\text{P})_2(\text{CO})(p\text{-tolN}(\text{YNR})\text{IrMCl})]$ (M = Cu, Ag, Y = CH, N, R = Me, Et, *i*-Pr)⁸ only one of the two possible isomers was observed except for R = Et, M = Cu, but the preference for the alkyl substituent to be bonded to the transition-metal site followed the same order as noted above:



Very likely, steric hindrance in these isostructural compounds, which have mutually trans Ph₃P ligands, will be much more important than that in the Pt–Ag complexes, in which two mutually trans NMe₂ groups are cis positioned with respect to the bridging ligand.

Conclusions

The electron-donating ability of Pt^{II} in nitrogen-coordinated organoplatinum(II) compounds has been shown to allow the formation of Pt^{II}-to-Ag^I donor bonds. Formamidino and triazenido ligands act as bridging ligands and as such have a greater stabilizing influence on the stability of the Pt-to-Ag bonds than isoelectronic carboxylato groups. With the latter ligands ligand-transfer products AgBr and $\{[2,6-(\text{Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3]\text{Pt}(\text{O}_2\text{CR})\}$ are obtained exclusively. Coordination of nonsymmetric bridging ligands *p*-tolN(YNR) can result in formation of two isomers, the relative ratio of which is very likely the result of electronic and steric factors in the intimate formation mechanism.

Acknowledgment. We thank Mr. J. M. Ernsting for technical assistance. Investigations were supported in part by the Netherlands Foundation for Chemical Research (SON), with financial aid from the Netherlands Organization for Pure Research (ZWO) (A.F.M.J.v.d.P.).

Registry No. [2,6-(Me₂NCH₂)₂C₆H₃][*p*-tolNC(H)NMe]PtAgBr, isomer A, 80484-86-2; [2,6-(Me₂NCH₂)₂C₆H₃][*p*-tolNC(H)NEt]PtAgBr, isomer A, 80484-87-3; [2,6-(Me₂NCH₂)₂C₆H₃][*p*-tolNC(H)N-*i*-Pr]PtAgBr, isomer A, 80484-88-4; [2,6-(Me₂NCH₂)₂C₆H₃][*p*-tolNC(H)N-*p*-tol]PtAgBr, 80484-89-5; [2,6-(Me₂NCH₂)₂C₆H₃](*p*-tolNNNMe)PtAgBr, isomer A, 80484-90-8; [2,6-(Me₂NCH₂)₂C₆H₃](*p*-tolNNNEt)PtAgBr, isomer A, 80484-91-9; [2,6-(Me₂NCH₂)₂C₆H₃](*p*-tolNNN-*i*-Pr)PtAgBr, isomer A, 80484-92-0; [2,6-(Me₂NCH₂)₂C₆H₃][*p*-tolNC(H)NMe]PtAgBr, isomer B, 80484-93-1; [2,6-(Me₂NCH₂)₂C₆H₃][*p*-tolNC(H)NEt]PtAgBr, isomer B, 80484-94-2; [2,6-(Me₂NCH₂)₂C₆H₃][*p*-tolNC(H)N-*i*-Pr]PtAgBr, isomer B, 80501-93-5; [2,6-(Me₂NCH₂)₂C₆H₃](*p*-tolNNNMe)PtAgBr, isomer B, 80484-95-3; [2,6-(Me₂NCH₂)₂C₆H₃](*p*-tolNNNEt)PtAgBr, isomer B, 80484-96-4; [2,6-(Me₂NCH₂)₂C₆H₃](*p*-tolNNN-*i*-Pr)PtAgBr, isomer B, 80484-97-5; [2,6-(Me₂NCH₂)₂C₆H₃]Pt(O₂CMe), 80484-98-6; [2,6-(Me₂NCH₂)₂C₆H₃]Pt(O₂C-*i*-Pr), 80484-99-7; [2,6-(Me₂NCH₂)₂C₆H₃]PtBr, 67507-09-9; Ag(*p*-tolNC(H)NMe), 72397-86-5; Ag(*p*-tolNC(H)NEt), 72397-87-6; Ag(*p*-tolNC(H)N-*i*-Pr), 72397-88-7; Ag(*p*-tolNC(H)N-*p*-tol), 72634-55-0; Ag(*p*-tolNNNMe), 74349-06-7; Ag(*p*-tolNNNEt), 74349-07-8; Ag(*p*-tolNNN-*i*-Pr), 80471-10-9.

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