Synthesis of Novel Terminal Iridium Phosphinidene Complexes

Arjan T. Termaten,[†] Tom Nijbacker,[†] Marius Schakel,[†] Martin Lutz,[‡] Anthony L. Spek,[‡] and Koop Lammertsma*[,†]

Department of Organic and Inorganic Chemistry, Faculty of Sciences, Vrije Universiteit, De Boelelaan 1083, NL-1081 HV, Amsterdam, The Netherlands, and Bijvoet Center for Biomolecular Research, Department of Crystal and Structural Chemistry, Utrecht University, Padualaan 8, NL-3584 CH, Utrecht, The Netherlands

Received January 29, 2002

Stable, crystalline iridium-complexed phosphinidenes, Cp*(L)Ir═PR, are readily synthesized by (a) the reaction of Cp*(L)$IrCl_2$ (**2**, L = PPh_3) with LiPHMes* and (b) dehydrohalogenation of Cp*(PH_2R)$IrCl_2$ (**5**, R = Mes*, Is, Mes) with in situ capturing of transient Cp*Ir≡PR (**4**) with phosphines, phosphites, arsines, isocyanides, and carbon monoxide (L). Cp*Ir≡PR eluded direct detection. The X-ray crystal structures are reported for Cp*(PPh_3)Ir═PMes* (**3**) and Cp*(CO)Ir═PMes* (**15**). The more congested **3** has an *E* configuration for its Ir═P bond, whereas **15** is obtained in its *Z* form. The ^{31}P NMR chemical shifts and $^2J_{PP}$ coupling constants are diagnostic for the *E* and *Z* forms. More shielded phosphinidene resonances and larger coupling constants are typical for the *E* isomers. These iridium-complexed phosphinidenes react with *gem*-diiodides to form phosphaalkenes, but not with carbonyl groups.

Introduction

Phosphinidenes stabilized by transition metal complexes, L_nM═PR, are attracting increased attention. These low-valent organophosphorus species are isolobal with the well-known carbene and imido complexes.[1] Likewise, they can be categorized into electrophilic or Fischer-type reagents, such as transient $(CO)_5M$═PR (M = Cr, Mo, W) and $(CO)_4Fe$═PN-*i*-Pr_2[2−4] and (stable) cationic [Cp*$(CO)_n$M = PN-*i*-Pr_2]$^+$ (*n* = 2, M = Ru; *n* = 3, M = Mo, W),[5] and into stable nucleophilic or Schrock-type reagents.[2] In 1987 Lappert et al.[6] reported the first such complexes for group 6 transition metals, i.e., Cp_2M═PR (M = Mo, W; R = Mes* (supermesityl; 2,4,6-tri-*tert*-butylphenyl), $CH(SiMe_3)_2$). Other nucleophilic complexes have been generated with transition metals from group 4 (Zr),[7] 5 (Ta),[8,9] and 6 (W)[10] and even an actinide (U).[11]

The reactivity of stable, isolated representatives of either Schrock- or Fischer-type phosphinidene complexes has hardly been explored, which is in sharp contrast with the wealth of novel (strained) organophosphorus compounds that could be synthesized from transient electrophilic species.[2−4] The most investigated species, zirconocene complex $Cp_2(PMe_3)$Zr═PMes*,[12] reacts, for example, like tantalum complex [N_3N]Ta═PR (N_3N = $(Me_3SiNCH_2CH_2)_3N$),[8] in a phospha-Wittig manner with aldehydes and ketones to give phosphaalkenes.

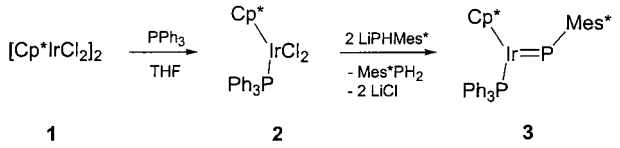
In our search to expand the availability of phosphinidenes, we were attracted to the late transition metals of group 9 (Co, Rh, Ir) to generate their yet unknown Cp(L)M═PR complexes. An extensive computational survey[13] suggests these to be less nucleophilic than the known metallocene-type complexes $Cp_2(PMe_3)$Zr═PMes*, Cp_2Mo═PMes*, and Cp_2W═PMes* when the stabilizing donor ligand L is a phosphine or CO. In the present study we focus on the transition metal iridium. Bergman et al.[14] reported earlier on the related, stable terminal imido complex Cp*Ir≡NR. The carbene analogue Cp*(PMe_3)Ir═CH_2 with an extra phosphine ligand is stable below −40 °C,[15] whereas the oxo-complex is stable as a dimer $[Cp^*IrO]_2$.[16] We will show convenient synthetic routes to Cp*(L)Ir═PR, report X-ray crystal

* Corresponding author. Tel: + 31-20-444-7474. Fax: + 31-20-444-7488. E-mail: lammert@chem.vu.nl.
[†] Vrije Universiteit.
[‡] Utrecht University.

(1) (a) Cowley, A. H.; Barron, A. R. *Acc. Chem. Res.* **1988**, *21*, 81−87. (b) Cowley, A. H. *Acc. Chem. Res.* **1997**, *30*, 445−451.
(2) Dillon, K. B.; Mathey, F.; Nixon, J. F. *Phosphorus: The Carbon Copy*; Wiley: Chichester, 1998; Chapter 3.
(3) Mathey, F. *Angew. Chem.* **1987**, *99*, 285−296; *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 275−286.
(4) (a) Wit, J. B. M.; van Eijkel, G. T.; de Kanter, F. J. J.; Schakel, M.; Ehlers, A. W.; Lutz, M.; Spek, A. L.; Lammertsma, K. *Angew. Chem.* **1999**, *111*, 2716−2719; *Angew. Chem., Int. Ed.* **1999**, *38*, 2596−2599. (b) Wit, J. B. M.; van Eijkel, G. T.; Schakel, M.; Lammertsma, K. *Tetrahedron* **2000**, *56*, 137−141.
(5) (a) Sterenberg, B. T.; Carty, A. J. *J. Organomet. Chem.* **2001**, *617−618*, 696−701. (b) Sterenberg, B. T.; Udachin, K. A.; Carty, A. J. *Organometallics* **2001**, *20*, 2657−2659.
(6) Hitchcock, P. B.; Lappert, M. F.; Leung, W. P. *J. Chem. Soc., Chem. Commun.* **1987**, 1282−1283.
(7) Hou, Z.; Breen, T. L.; Stephan, D. W. *Organometallics* **1993**, *12*, 3158−3167.
(8) Cummins, C. C.; Schrock, R. R.; Davis, W. M. *Angew. Chem.* **1993**, *105*, 758−761.
(9) Bonanno, J. B.; Wolckzanski, P. T.; Lobkovsky, E. B. *J. Am. Chem. Soc.* **1994**, *116*, 11159−11160.
(10) Cowley, A. H.; Pellerin, B. *J. Am. Chem. Soc.* **1990**, *112*, 6734−6735.
(11) Arney, D. S. J.; Schnabel, R. C.; Scott, B. C.; Burns, C. J. *J. Am. Chem. Soc.* **1996**, *118*, 6780−6781.
(12) Breen, T. L.; Stephan, D. W. *J. Am. Chem. Soc.* **1995**, *117*, 11914−11921.
(13) Ehlers, A. W.; Baerends, E.-J.; Lammertsma, K. *J. Am. Chem. Soc.* **2002**, *124*, 2831−2838.
(14) Glueck, D. S.; Wu, J.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1991**, *113*, 2041−2054.
(15) Klein, D. P.; Bergman, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 3079−3080.

10.1021/om020062t CCC: $22.00
Publication on Web 06/25/2002

Scheme 1



1 **2** **3**

structures for two of them, and demonstrate their nucleophilic character.

Results and Discussion

Iridium-complexed phosphinidenes can be formed from Cp*(L)$IrCl_2$ (**2**, L = PPh_3) by reaction with lithium phosphides and in a more versatile manner by dehydrohalogenation with simultaneous ligand addition.

A. Lithium Phosphide Route. Complex **2** is readily prepared from the $[Cp^*IrCl_2]_2$ dimer (**1**) and triphenylphosphine in THF.[17] Subsequent addition at room temperature of 2 equiv of LiPHMes*·3THF in toluene results in formation of phosphinidene complex **3**, Mes*PH_2 (liberated during reaction), and other organophosphorus products, among which is diphosphine Mes*PH−PHMes* (Scheme 1). The presence of **3** is evident from its ^{31}P NMR chemical shifts at δ 687 and 25, and the large $^2J_{PP}$ coupling constant between the ^{31}P nuclei of 102 Hz; the low-field resonance is characteristic for a bent terminal phosphinidene complex.[1b] Phosphinidene complex **3** was isolated in 43% yield as stable, mildly air-sensitive, dark green crystals.

The crystal structure of **3** confirms it to be a monomeric, terminal phosphinidene complex in which the large groups around the Ir═P(1) bond are in an anti or *E* configuration (Figure 1); selected bond distances and angles are listed in Table 1. The two-legged piano stool geometry of **3** has an acute P(1)−Ir(1)−P(2) angle of 86.563(19)° between its two legs. The distortion from planarity of the phenyl ring of the supermesityl group may result from repulsion between the bulky Cp* and ortho *tert*-butyl groups.

The 2.2121(5) Å Ir(1)−P(1) bond distance is short compared to the 2.324 Å for the Ir−PPh_3 bond of **2**[18] and indicates double-bond character in accordance with a recent theoretical survey on phosphinidene complexes.[13] The Ir═P nature is further supported by the Ir(1)−P(1)−C(1) angle of 113.73(7)°, which is typical for a bent phosphinidene complex.[6,7] Interestingly, the 2.2483(5) Å Ir(1)−P(2) distance for the Ir−PPh_3 bond of **3** is only marginally longer than the Ir(1)−P(1) phosphinidene bond and shows the triphenylphosphine group to have a much stronger stabilizing effect than it has in **2**.

Attempts to synthesize Cp*Ir≡PR (**4**), free of the stabilizing PPh_3 ligand, in analogy with the reported imido complex,[14] were unsuccessful. Reaction of $[Cp^*IrCl_2]_2$ (**1**) with lithium phosphide LiPHR·*n*THF (R = Mes*, Mes) led to a mixture of unidentifiable products. Apparently, Cp*Ir≡PR is significantly less stable than its imido analogue.

B. Dehydrohalogenation−Ligand Addition Route. Whereas Cp*Ir≡PR (**4**) eludes direct detection, it may serve as a synthon for generating phosphinidene complexes. Therefore, we decided to probe its access by dehydrohalogenation of novel primary phosphine complexes Cp*Ir(PH_2R)Cl_2 (**5**) and immediately capturing transient **4** with a stabilizing transition metal ligand. This method proved to be both successful and general, because of the diversity of ligands that can be used. We investigated the reaction for the ligands PMe_3, PPh_3, PH_2Mes*, $P(OMe)_3$, dppe, $AsPh_3$, *t*-BuNC, XyNC, and CO, all of which give yields of the complexed phosphinidene (**3**, **6**−**15**) of 80% or more (Table 2).

Dehydrohalogenation of **5a**, formed from $[Cp^*IrCl_2]_2$ and primary phosphine PH_2Mes*, with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in the presence of PPh_3 gives phosphinidene **3** in 86% isolated yield (entry 1), thereby demonstrating the superiority of this method over that of the lithium phosphide route. Using the smaller isityl (Is; 2,4,6-tri-isopropylphenyl) and mesityl (Mes) groups in complexes **5b** and **5c**, respectively, results likewise in the corresponding phosphinidene complexes **6** (entry 2) and **7** (entry 3). These have characteristic low-field ^{31}P NMR chemical shifts for their phosphinidene phosphorus atom similar to **3** albeit that they are slightly more shielded, i.e., δ 664 for **6** and δ 652 for **7** vs δ 687 for **3**. The large $^2J_{PP}$ coupling constants of **6** (77 Hz) and **7** (75 Hz) suggest these structures to have an *E* configuration like that of the more congested **3** (102 Hz). However, executing the reaction with the unsubstituted phenyl group, i.e., Cp*Ir(PH_2Ph)Cl_2,[19] results only in unidentifiable products. Evidently, the size of the phosphinidene substituent is important. Throughout the rest of the study we used the Mes* group as the substituent at phosphorus, i.e., **5a**.

Reaction of **5a** with DBU in the absence of a phosphine results mostly in unidentifiable products, thereby illustrating that Cp*Ir≡PMes* (**4a**) itself is unstable under the reaction conditions.[20]

We next explored the use of smaller phosphine ligands. Dehydrohalogenating **5a** with DBU in the presence of primary phosphine PH_2Mes* results in phosphinidene complex **8** in 85% yield (entry 4). Characteristic are the low-field ^{31}P NMR resonance at δ 715 ($^2J_{PP}$ = 20 Hz) for its phosphinidene group and the high-field resonance for the primary phosphine ligand at δ = −84 ($^1J_{PH}$ = 384 Hz), which resembles that of **5a** (δ −57.1, $^1J_{PH}$ = 397 Hz). Because the $^2J_{PP}$ coupling constant is 82 Hz smaller than that of **3**, and since the PH_2Mes* ligand is far less bulky than PPh_3 (especially when the Mes* group is rotated away), we presume **8** to have the less congested *Z* or syn configuration. Evidently, the preference for an *E* or *Z* orientation of

(16) McGhee, W. D.; Foo, T.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 8543−8545.

(17) Kang, J. W.; Mosely, K.; Maitlis, P. M. *J. Am. Chem. Soc.* **1969**, *91*, 5970−5977.

(18) Le Bras, J.; Amouri, H.; Vaissermann, J. *J. Organomet. Chem.* **1997**, *548*, 305−307.

(19) Esteban, M.; Pequerul, A.; Carmona, D.; Lahoz, F. J.; Martín, A.; Oro, L. A. *J. Organomet. Chem.* **1991**, *402*, 421−434.

(20) The first dehydrohalogenation to Cp*(Cl)Ir═PHMes* using 1 equiv of DBU was confirmed at temperatures below 0 °C by the presence of resonances at δ 117 ($^1J_{PH}$ = 404 Hz) and 128 ($^1J_{PH}$ = 363 Hz) in a ratio of 85:15 in the ^{31}P NMR spectrum of the complex reaction mixture. Ligand addition to this phosphide complex with subsequent dehydrohalogenation of Cp*(L)(Cl)Ir═PHMes* will also render phosphinidene complexes, as suggested by a referee. This alternative route cannot be excluded and may, in fact, compete with the didehydrohalogenation−ligation sequence. Because in the presence of PPh_3 ^{31}P NMR resonances are also observed below 0 °C at δ 480−630, we conclude that free and/or solvent-complexed Cp*Ir═PMes* is a major reactive intermediate in the reaction mixture.

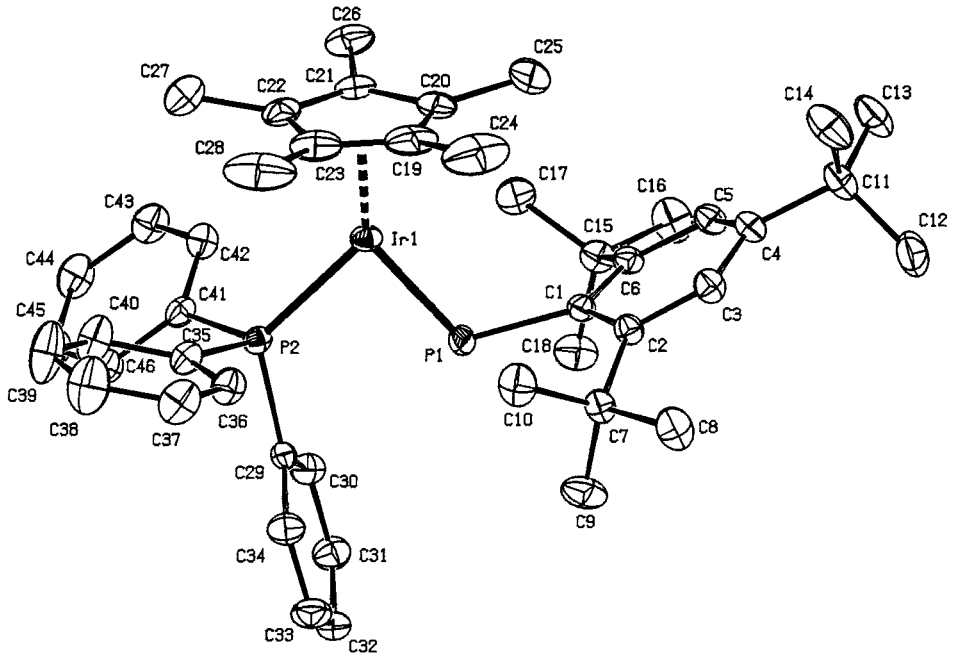


Figure 1. Displacement ellipsoid plot (50% probability level) of **3**. Hydrogen atoms are omitted for clarity.

Table 1. Selected Bond Distances (Å), Angles (deg), and Torsion Angles (deg) for Cp*(PPh$_3$)Ir=PMes* (3)

Ir(1)−P(1)	2.2121(5)	Ir(1)−P(1)−C(1)	113.73(7)
Ir(1)−P(2)	2.2483(5)	P(1)−Ir(1)−Cp(cg)	143.05(4)
Ir(1)−Cp(cg)	1.9227(12)	P(1)−Ir(1)−P(2)	86.563(19)
P(1)−C(1)	1.858(2)	P(2)−Ir(1)−Cp(cg)	130.39(4)
P(2)−C(29)	1.839(2)	C(6)−C(1)−C(2)−C(3)	14.8(3)
P(2)−C(35)	1.833(2)	C(2)−C(1)−C(6)−C(5)	−14.1(3)
P(2)−C(41)	1.842(2)		

the phosphinidene complex is rather sensitive to the steric size of the ligand, with larger ones enforcing the formation of the *E* form. This is further illustrated in the next two examples.

Introduction of PMe_3, which is also smaller than PPh_3, results in the formation of two isomers of **9** in 85% yield (entry 5). We assign the *E* configuration to the major isomer (92%) on the basis of its phosphinidene resonance at δ 629 and the large $^2J_{PP}$ coupling constant of 84 Hz. The minor *Z* isomer has a much more deshielded ^{31}P chemical shift for the phosphinidene at δ 727 and a much smaller $^2J_{PP}$ coupling constant of 18 Hz, both resembling those of **8**.

Two isomers (**10**) are also formed with trimethyl phosphite ($P(OMe)_3$; entry 6). In this case the major isomer (96%) has instead the *Z* configuration, which we base on its very low-field ^{31}P NMR chemical shift at δ 797 and small $^2J_{PP}$ coupling constant of 9 Hz; the minor *E* isomer, with an ^{31}P NMR chemical shift at δ 680, also has a rather small $^2J_{PP}$ of 20 Hz.

Performing the dehydrohalogenation of **5a** in the presence of 0.5 equiv of 1,2-bis(diphenylphosphino)-ethane (dppe), an established dichelating ligand, affords dinuclear phosphinidene complex **11**, $(Cp^*Ir{=}PMes^*)_2$-(dppe), in a surprisingly good yield of 82% (entry 7). Both phosphine groups of dppe serve as a stabilizing ligand but to different iridium atoms. The single low-field ^{31}P NMR chemical shift at δ 655 and $^2J_{PP}$ coupling constant of 69 Hz suggest that both phosphinidene units have an *E* configuration for their Ir=P bonds. Performing the reaction with 1.2 equiv of dppe results in a mixture of the mononuclear Cp*(dppe)Ir=PMes* complex and dinuclear **11** in a ratio of 3:2. Expectedly, the mononuclear product also has an *E* configuration, on the basis of its ^{31}P NMR chemical shift at δ 655.9 and $^2J_{PP}$ value of 83 Hz. We were unable to isolate the mononuclear product from the reaction mixture, even when a larger access of dppe was used.

Non-phosphorus-containing ligands were probed next. Using triphenylarsine, the heavier congener of PPh_3, results in **12** (93%, entry 8), which we assume to have an *E* configuration on the basis of its ^{31}P NMR chemical shift at δ 655, which is similar to that of **3**. Stable products are also obtained with isocyanide ligands. The *tert*-butyl derivative gives phosphinidene complex **13** (91%, entry 9), which we speculate to have a *Z* configuration on the basis of its low-field ^{31}P NMR chemical shift at δ 740. Likewise, the xylyl derivative gives phosphinidene **14**, which has a similar ^{31}P NMR chemical shift at δ 757 (93%, entry 10).

Finally, a CO ligand was introduced by leading gaseous carbon monoxide though the dehydrohalogenating reaction mixture of **5a** to give deep red colored phosphinidene **15** (88%, entry 11). The complex has a strong IR absorption at 1968 cm^{-1}, which is typical for a terminal CO ligand. Its very deshielded ^{31}P NMR chemical shift at δ 805 suggests a *Z* configuration, which was confirmed by a single-crystal X-ray structure determination (Figure 2, Table 3). The structure has a crystallographic mirror plane through C(15), C(12), Ir(1), C(18), O(1), P(1), C(1), C(4), C(9), and C(11). The P(1)−Ir(1)−C(18) angle of 94.29(13)° between the two legs of the piano stool is wider than in **3** and is attributed to the close proximity of the Mes* substituent to the CO ligand. The Ir−P(1)−C(1) angle of 113.77(10)° is remarkably similar to that of **3** and may reflect the effect of the bulky Mes* group. The Ir(1)−P(1) distance of 2.1783(8) Å is significantly shorter than in **3**, which may have its origin in their different configurations (*E* for **3** and *Z* for **15**) and/or in the different ligand stabilization (PPh_3 for **3** and CO for **15**). Phosphinidene

Table 2. Iridium Phosphinidene Complexes[a]

entry	R	L	product	yield (%)	δ ^{31}P (ppm)[b]	$^{2}J_{PP}$ (Hz)
1	Mes*	PPh_3	Cp*(PPh_3)Ir=PMes* (**3**)	86	687	102
2	Is	PPh_3	Cp*(PPh_3)Ir=PIs (**6**)	80	664	77
3	Mes	PPh_3	Cp*(PPh_3)Ir=PMes (**7**)	83	652	75
4	Mes*	PH_2Mes*	Cp*(PH_2Mes*)Ir=PMes* (**8**)	85	715	20
5	Mes*	PMe_3	Cp*(PMe_3)Ir=PMes* (**9**)	85	629 (92%)	84
					727 (8%)	18
6	Mes*	$P(OMe)_3$	Cp*($P(OMe)_3$)Ir=PMes* (**10**)	94	680 (4%)	20
					797 (96%)	9
7	Mes*	dppe	(Cp*Ir=PMes*)$_2$(dppe) (**11**)	82	655	69
8	Mes*	$AsPh_3$	Cp*($AsPh_3$)Ir=PMes* (**12**)	93	655	
9	Mes*	*t*-BuNC	Cp*(*t*-BuNC)Ir=PMes* (**13**)	91	740	
10	Mes*	XyNC	Cp*(XyNC)Ir=PMes* (**14**)	93	757	
11	Mes*	CO	Cp*(CO)Ir=PMes* (**15**)	88	805	

[a] Cp* = 1,2,3,4,5-pentamethylcyclopentadienyl; Ph = phenyl; Me = methyl; Xy = 2,6-dimethylphenyl; Mes = 2,4,6-trimethylphenyl; Is = 2,4,6-tri-isopropylphenyl; Mes* = 2,4,6-tri-*tert*-butylphenyl; dppe = 1,2-bis(diphenylphosphino)ethane. [b] In C_6D_6 as solvent.

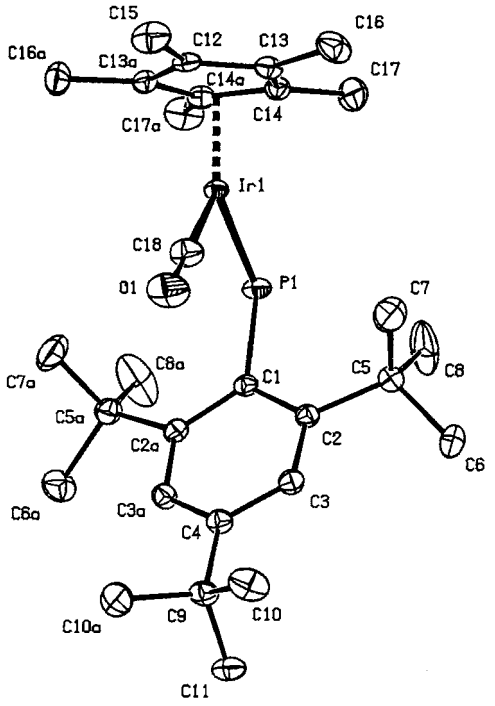


Figure 2. Displacement ellipsoid plot (50% probability level) of **15**. Hydrogen atoms are omitted for clarity (symmetry operation: x, 0.5 − y, z).

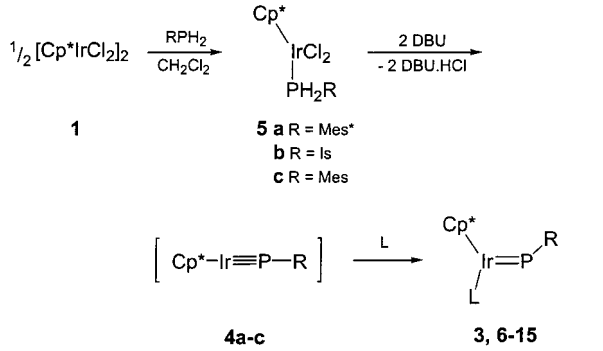
Table 3. Selected Bond Distances (Å), Angles (deg), and Torsion Angles (deg) for Cp*(CO)Ir=PMes* (15)

Ir(1)−P(1)	2.1783(8)	Ir(1)−P(1)−C(1)	113.77(10)
Ir(1)−Cp(cg)	1.9132(10)	Ir(1)−C(18)−O(1)	179.2(4)
Ir(1)−C(18)	1.849(3)	P(1)−Ir(1)−Cp(cg)	128.65(4)
P(1)−C(1)	1.849(3)	P(1)−Ir(1)−C(18)	94.29(13)
C(18)−O(1)	1.142(4)	C(18)−Ir(1)−Cp(cg)	137.07(13)
		C(2a)−C(1)−C(2)−C(3)	−10.2(4)

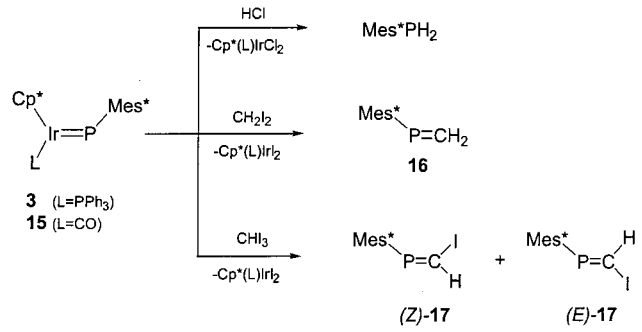
15 is the first Schrock-type complex to have a Cp* and CO ligand at the transition metal.

C. Reactivities. Small-scale experiments were performed for **3** and **15** to explore their reactivity (Scheme 3). No reactions were observed with carbonyl compounds such as benzaldehyde and acetone, neither at ambient nor at elevated temperatures. This behavior contrasts that of the "phospha-Wittig" reactivity of $Cp_2(PMe_3)$-Zr=PMes* and (N_3N)Ta=PR that enables the conversion of carbonyl compounds into phosphaalkenes.[8,12] However, the results are in line with a recent theoretical study that predicts a decreased nucleophilicity for iridium-complexed phosphinidenes.[13] The lower oxophilicity of iridium than either the zirconium or tantalum transition metal complexes may also be a contributing factor.[21]

Scheme 2



Scheme 3



Phosphinidenes **3** and **15** are sensitive toward acids. Addition of HCl results in the rapid formation of Cp*Ir-(L)Cl_2 and Mes*PH_2. In contrast to $Cp_2(PMe_3)$Zr= PMes*, neither reacts with simple *gem*-dichlorides, such as CH_2Cl_2 and $CHCl_3$, but transfer of the phosphinidene unit does occur with *gem*-diiodides. Thus, **3** reacts slowly at 60 °C with CH_2I_2 to give the known phosphaalkene **16**[22] and Cp*Ir(PPh_3)I_2 (the diiodo analogue of **3**), whereas the same reaction using **15** occurs already at room temperature. Both phosphinidene complexes react cleanly with CHI_3 to give a 3:1 mixture of the *Z* and *E* isomers of the known phosphaalkene **17**,[23] again with the reaction using **15** being the fastest. We speculate that this difference in behavior between **3** and **15** may be of a steric nature (*E* vs *Z* and PPh_3 vs CO), although

(21) Nugent, W. A.; Mayer, J. M. *Metal−Ligand Multiple Bonds*; Wiley: New York, 1989.

differences in electronic character (charge on P and strength of the Ir=P bond) may contribute. These aspects are a topic of future study.

Conclusions

In this paper, two synthetic routes toward novel iridium phosphinidene complexes are described. One uses the reaction of $Cp^*(L)IrCl_2$ (**2**) with LiPHMes*, which we investigated for L = PPh_3. The other more versatile, high-yielding, and thereby superior method employs dehydrohalogenation of $Cp^*(PH_2R)IrCl_2$ (**5**) with in situ capturing of transient Cp*Ir≡PR (**4**) with stabilizing ligands, such as phosphines, phosphites, arsines, isocyanides, and carbon monoxide. Attempts to detect Cp*Ir≡PR (**4**) were unsuccessful. The X-ray crystal structures for $Cp^*(PPh_3)Ir{=}PMes^*$ (**3**) and Cp*(CO)Ir=PMes* (**15**) showed the Ir=P bond of these phosphinidene complexes to have *E* and *Z* configurations, respectively. The ^{31}P NMR chemical shifts of the phosphinidene phosphorus of **3** and **6**−**15**, and where applicable the magnitude of the $^2J_{PP}$ coupling constant, are diagnostic for the *E* and *Z* forms. The *Z* form is preferred with smaller ligands and the *E* form with bulky ones.

Phosphinidene complexes **3** and **15** are unreactive toward carbonyl groups. Phosphaalkenes are obtained in the reaction of **3** and **15** with *gem*-diiodides, such as CH_2I_2 and CHI_3, and "re-formation" of PH_2Mes^* and $Cp^*Ir(L)Cl_2$ occurs on treatment with HCl. The reactivity of **15** is slightly higher than that of **3**.

Experimental Section

General Data. All experiments were performed in flame-dried glassware and under an atmosphere of dry nitrogen or argon. Solvents were distilled (under N_2) from sodium (toluene), sodium benzophenone (THF), diphosphoruspentoxide (CH_2Cl_2, $CHCl_3$), or lithium aluminum hydride (*n*-pentane, *n*-hexane). Deuterated solvents were dried over 4 Å molecular sieves ($CDCl_3$, C_6D_6). All solid starting materials were dried in vacuo. ^1H, ^{13}C, and ^{31}P NMR spectra were recorded at 300 K on a Bruker Avance 250 spectrometer at 250.13, 62.90, and 101.25 MHz, respectively. ^1H NMR spectra were referenced to $CHCl_3$ (δ 7.27 ppm) or C_6D_5H (δ 7.17 ppm), ^{13}C NMR spectra to $CDCl_3$ (δ 77.16 ppm) or C_6D_6 (δ 128.06 ppm), and ^{31}P NMR spectra to external 85% H_3PO_4. IR spectra were recorded on a Mattson-6030 Galaxy FTIR spectrophotometer, and high-resolution mass spectra (HRMS) on a Finnigan Mat 900 spectrometer. Elemental analyses were performed by Mikroanalytisches Labor Pascher, Remagen-Bandorf, Germany. $[Cp^*IrCl_2]_2$,[24] $Cp^*(PPh_3)IrCl_2$,[17] $IsPH_2$,[25] Mes^*PH_2,[26] and LiPHMes*·3THF[7] were prepared according to literature procedures. $MesPH_2$ was prepared, analogously to $IsPH_2$, by $LiAlH_4$ reduction of $MesPCl_2$.[27]

[Cp*(PPh$_3$)Ir=PMes*] (3). A freshly prepared solution of LiPHMes*·3THF (1.0 g, 2.0 mmol) in toluene (20 mL) was added slowly to an orange suspension of **2** (0.66 g, 1.0 mmol) in toluene (10 mL) and stirred overnight. After removal of the solvent the brown-green residue was extracted into *n*-pentane (50 mL) and filtered to remove LiCl. After removal of the solvent, the residue was washed with cold *n*-pentane (10 mL) to remove Mes^*PH_2 and crystallized from toluene/*n*-pentane at −20 °C to give large green-black crystals of **3** (376 mg, 0.43 mmol, 43%). Mp: 222−224 °C. ^{31}P NMR (C_6D_6): δ 686.6 (d, $^2J_{PP}$ = 102 Hz, Ir=P), 24.8 (d, $^2J_{PP}$ = 102 Hz, Ir−PPh_3). ^1H NMR (C_6D_6): δ 1.34 (d, $^4J_{PC}$ = 1.30 Hz, 15H, $C_5(CH_3)_5$), 1.51 (s, 9H, *p*-$C(CH_3)_3$), 1.61 (s, 18H, *o*-$C(CH_3)_3$), 7.07−7.19 (m, 9H, PPh_3), 7.48 (s, 2H, *m*-Mes*), 7.92 (m, 6H, PPh_3). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 9.75 (s, $C_5(CH_3)_5$), 32.2 (s, *o*-$C(CH_3)_3$), 32.3 (s, *p*-$C(CH_3)_3$), 34.6 (s, *p*-$C(CH_3)_3$), 38.5 (s, *o*-$C(CH_3)_3$), 94.0 (d, $^2J_{PC}$ = 3.7 Hz, $C_5(CH_3)_5$), 120.5 (s, *m*-Mes*), 127.1 (d, $^3J_{PC}$ = 10.0 Hz, *m*-PPh_3), 129.2 (d, $^4J_{PC}$ = 2.2 Hz, *p*-PPh_3), 135.6 (d, $^2J_{PC}$ = 10.5 Hz, *o*-PPh_3), 136.8 (d, $^1J_{PC}$ = 52.7 Hz, *i*-PPh_3), 145.3 (s, *o*-Mes*), 145.9 (s, *p*-Mes*), 168.6 (dd, $^1J_{PC}$ = 106 Hz, $^3J_{PC}$ = 21.1, *i*-Mes*). HRMS: calcd for $C_{46}H_{59}P_2Ir$ 866.37207; found 866.37055.

[Cp*(PH$_2$Mes*)IrCl$_2$] (5a). Mes^*PH_2 (0.21 g, 0.75 mmol) was added to a dark orange solution of $[Cp^*IrCl_2]_2$ (0.25 g, 0.31 mmol) in CH_2Cl_2 (25 mL), which was stirred for 4 h at 40 °C and filtered to remove insoluble material. After concentrating the solution, *n*-pentane (30 mL) was added slowly to cause precipitation of an orange crystalline product, which was isolated by filtration, washed with *n*-pentane (25 mL), and dried in vacuo to give **5a** (0.33 g, 0.49 mmol, 79%). Mp: 219−220 °C (dec). ^{31}P NMR ($CDCl_3$): δ −57.1 (t, $^1J_{PH}$ = 397 Hz). ^1H NMR ($CDCl_3$): δ 1.32 (s, 9H, *p*-$C(CH_3)_3$), 1.33 (d, $^4J_{PH}$ = 1.0 Hz, 15H, $C_5(CH_3)_5$), 1.55 (s, 18H, *o*-$C(CH_3)_3$), 6.76 (d, $^1J_{PH}$ = 397 Hz, 2H, PH_2), 7.49 (d, $^4J_{PH}$ = 2.8 Hz, 2H, *m*-Mes*). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 8.50 (d, $^3J_{PC}$ = 0.8 Hz, $C_5(CH_3)_5$), 31.1 (s, *p*-$C(CH_3)_3$), 33.0 (d, $^4J_{PC}$ = 1.5 Hz, *o*-$C(CH_3)_3$), 34.9 (s, *p*-$C(CH_3)_3$), 38.0 (d, $^3J_{PC}$ = 2.2 Hz, *o*-$C(CH_3)_3$), 91.8 (d, $^2J_{PC}$ = 3.3 Hz, $C_5(CH_3)_5$), 115.7 (d, $^1J_{PC}$ = 38.6 Hz, *i*-Mes*), 122.3 (d, $^3J_{PC}$ = 10.0 Hz, *m*-Mes*), 152.4 (s, *p*-Mes*), 155.8 (d, $^2J_{PC}$ = 5.2 Hz, *o*-Mes*). IR (KBr, cm^{-1}): ν(PH) 2421, 2376. HRMS: calcd for $C_{28}H_{46}PCl_2Ir$ 676.23431; found 676.23327. Anal. Calcd for $C_{28}H_{46}PCl_2Ir$: C, 49.69; H, 6.86; P, 4.58. Found: C, 49.59; H, 6.68; P, 4.68.

[Cp*(PH$_2$Is)IrCl$_2$] (5b). In a fashion similar to that described for **5a**, $IsPH_2$ (0.18 g, 0.75 mmol) was used to give orange crystals of **5b** (0.34 g, 0.54 mmol, 87%). Mp: 210−212 °C (dec). ^{31}P NMR ($CDCl_3$): δ −76.8 (triplet, $^1J_{PH}$ = 395 Hz). ^1H NMR ($CDCl_3$): δ 1.25 (d, $^3J_{HH}$ = 6.9 Hz, 6H, *p*-$CH(CH_3)_2$), 1.30 (d, $^3J_{HH}$ = 6.6 Hz, 12H, *o*-$CH(CH_3)_2$), 1.58 (d, $^4J_{PH}$ = 2.7 Hz, 15H, $C_5(CH_3)_5$), 2.90 (sep, $^3J_{HH}$ = 6.9 Hz, 1H, *p*-$CH(CH_3)_2$), 3.18 (sep, $^3J_{HH}$ = 6.6 Hz, 2H, *o*-$CH(CH_3)_2$), 5.83 (d, $^1J_{PH}$ = 395 Hz, 2H, PH_2), 7.08 (d, $^4J_{PH}$ = 3.3 Hz, 2H, *m*-Is). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 8.73 (s, $C_5(CH_3)_5$), 24.0 (s, *p*-$CH(CH_3)_2$), 24.4 (s, *o*-$CH(CH_3)_2$), 32.2 (d, $^3J_{PC}$ = 9.5 Hz, *o*-$CH(CH_3)_2$), 34.5 (s, *p*-$CH(CH_3)_2$), 92.3 (d, $^2J_{PC}$ = 3.2 Hz, $C_5(CH_3)_5$), 114.1 (d, $^1J_{PC}$ = 52.9 Hz, *i*-Is), 121.8 (d, $^3J_{PC}$ = 8.3 Hz, *m*-Is), 152.8 (d, $^4J_{PC}$ = 2.4 Hz, *p*-Is), 153.0 (d, $^2J_{PC}$ = 7.4 Hz, *o*-Is). IR (KBr, cm^{-1}): ν(PH) 2400, 2371. HRMS: calcd for $C_{25}H_{40}PCl_2Ir$ 634.18738; found 634.18513.

[Cp*(PH$_2$Mes)IrCl$_2$] (5c). In a fashion similar to that described for **5a**, $MesPH_2$ (0.10 g, 0.66 mmol) was used to give orange crystals of **5c** (0.25 g, 0.45 mmol, 73%), which retained a small amount of CH_2Cl_2 (0.2 equiv). Mp: 228−230 °C (dec). ^{31}P NMR ($CDCl_3$): δ −75.1 (triplet, $^1J_{PH}$ = 398 Hz). ^1H NMR ($CDCl_3$): δ 1.55 (d, $^4J_{PH}$ = 2.6 Hz, 15H, $C_5(CH_3)_5$), 2.34 (s, 3H, *p*-CH_3), 2.42 (s, 6H, *o*-CH_3), 5.85 (d, $^1J_{PH}$ = 397.7 Hz, 2H, PH_2), 6.97 (d, $^4J_{PH}$ = 2.7 Hz, 2H, *m*-Mes). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 8.53 (s, $C_5(CH_3)_5$), 21.3 (s, *p*-CH_3), 22.1 (d, $^3J_{PC}$ = 8.9 Hz, *o*-CH_3), 92.3 (d, $^2J_{PC}$ = 3.3 Hz, $C_5(CH_3)_5$), 116.6 (d, $^1J_{PC}$ = 51.3 Hz, *i*-Mes), 129.5 (d, $^3J_{PC}$ = 8.3 Hz, *m*-Mes), 141.4 (d, $^4J_{PC}$ = 2.5 Hz, *p*-Mes), 142.1 (d, $^2J_{PC}$ = 7.7 Hz, *o*-Mes). IR (KBr, cm^{-1}):

(22) Appel, R.; Casser, C.; Immenkeppel, M.; Knoch, F. *Angew. Chem.* **1984**, *96*, 905−906; *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 895−896.

(23) (a) Appel, R.; Immenkeppel, M. *Z. Anorg. Allg. Chem.* **1987**, *553*, 7−14. (b) Goede, S.; Bickelhaupt, F. *Chem. Ber.* **1991**, *124*, 2677−2684.

(24) White, C.; Yates, A.; Maitlis, P. M. *Inorg. Synth.* **1992**, *29*, 228−234.

(25) van den Winkel, Y.; Bastiaans, H. M. M.; Bickelhaupt, F. *J. Organomet. Chem.* **1991**, *405*, 183−194.

(26) Cowley, A. H.; Kilduff, J. E.; Newman, T. H.; Pakulski, M. *J. Am. Chem. Soc.* **1982**, *104*, 5820−5821.

(27) Nief, F.; Mathey, F. *Tetrahedron* **1991**, *47*, 6673−6680.

ν(PH) 2396, 2346. Anal. Calcd for $C_{19}H_{28}PCl_2Ir\cdot 0.2CH_2Cl_2$: C, 40.64; H, 5.05; P, 5.46. Found: C, 40.30; H, 4.87; P, 5.48.

[Cp*(PPh$_3$)Ir=PMes*] (3) from 5a. A yellow-orange solution of **5a** (135 mg, 0.20 mmol) in CH_2Cl_2 (2.5 mL) was added dropwise to a solution of DBU (59.8 μL, 0.40 mmol) and PPh_3 (52.5 mg, 0.20 mmol) in toluene (5 mL) and stirred for an additional 5 min. After removal of the solvents the residue was extracted with *n*-pentane (25 mL), filtered, and concentrated to give **3** (149 mg, 0.172 mmol, 86%). The spectroscopic data are identical to those described above. The same procedure was used to prepare compounds **6**−**15**.

[Cp*(PPh$_3$)Ir=PIs] (6). 6 was prepared from **5b** (127 mg, 0.20 mmol), DBU (59.8 μL, 0.40 mmol), and PPh_3 (52.5 mg, 0.20 mmol) to give dark orange-red crystals (131 mg, 0.159 mmol, 80%). Mp: 140−142 °C. ^{31}P NMR (C_6D_6): δ 663.8 (d, $^2J_{PP}$ = 77 Hz, Ir=P), 27.3 (d, $^2J_{PP}$ = 77 Hz, Ir−PPh$_3$). ^{1}H NMR ($CDCl_3$): δ 1.15 (d, $^3J_{HH}$ = 6.7 Hz, 6H, *o*-CH(CH_3)$_2$), 1.42 (d, $^3J_{HH}$ = 6.9 Hz, 6H, *p*-CH(CH_3)$_2$), 1.46 (d, $^4J_{PH}$ = 1.1 Hz, 15H, C$_5$(CH_3)$_5$), 1.57 (d, $^3J_{HH}$ = 6.8 Hz, 6H, *o*-CH(CH_3)$_2$), 3.02 (sep, $^3J_{HH}$ = 6.9 Hz, 1H, *p*-C*H*(CH$_3$)$_2$), 3.57 (sep, $^3J_{HH}$ = 6.8 Hz, 2H, *o*-C*H*(CH$_3$)$_2$), 7.00−7.15 (m, 9H, PPh$_3$), 7.13 (s, 2H, *m*-Is), 7.92−7.99 (m, 6H, PPh$_3$). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 9.44 (s, C$_5$(*C*H$_3$)$_5$), 23.2 (s, *p*-CH(*C*H$_3$)$_2$), 24.7 (bs, *o*-CH(*C*H$_3$)$_2$), 25.0 (s, *o*-CH(*C*H$_3$)$_2$), 30.1 (bs, *o*-*C*H(CH$_3$)$_2$), 34.9 (s, *p*-*C*H(CH$_3$)$_2$), 93.6 (d, $^2J_{PC}$ = 3.8 Hz, *C*$_5$(CH$_3$)$_5$), 119.6 (s, *m*-Is), 127.3 (d, $^3J_{PC}$ = 10.1 Hz, *m*-PPh$_3$), 129.4 (d, $^4J_{PC}$ = 2.2 Hz, *p*-PPh$_3$), 135.8 (d, $^2J_{PC}$ = 10.7 Hz, *o*-PPh$_3$), 137.1 (d, $^1J_{PC}$ = 52.0 Hz, *i*-PPh$_3$), 143.6 (s, *o*-Is), 146.9 (s, *p*-Is). HRMS: calcd for $C_{43}H_{53}P_2Ir$ 824.32513; found 824.32622.

[Cp*(PPh$_3$)Ir=PMes] (7). 7 was prepared from **5c** (110 mg, 0.20 mmol), DBU (59.8 μL, 0.40 mmol), and PPh_3 (52.5 mg, 0.20 mmol) to give dark orange-red crystals (123 mg, 0.166 mmol, 83%). Mp: 165−167 °C. ^{31}P NMR (C_6D_6): δ 651.8 (d, $^2J_{PP}$ = 75 Hz, Ir=P), 27.9 (d, $^2J_{PP}$ = 75 Hz, Ir−PPh$_3$). ^{1}H NMR (C_6D_6): δ 1.42 (d, $^4J_{PH}$ = 1.46 Hz, 15H, C$_5$(CH_3)$_5$), 2.31 (s, 6H, *o*-CH$_3$), 2.39 (s, 3H, *p*-CH$_3$), 6.85 (bs, 2H, *m*-Mes), 7.03−7.19 (m, 9H, PPh$_3$), 7.89−7.97 (m, 6H, PPh$_3$). ^{13}C{^{1}H} NMR (C_6D_6): δ 9.33 (d, $^3J_{PC}$ = 0.5 Hz, C$_5$(*C*H$_3$)$_5$), 19.9 (d, $^3J_{PC}$ = 6.4 Hz, *o*-*C*H$_3$), 21.2 (s, *p*-*C*H$_3$), 93.7 (d, $^2J_{PC}$ = 3.7 Hz, *C*$_5$(CH$_3$)$_5$), 127.4 (d, $^3J_{PC}$ = 10.1 Hz, *m*-PPh$_3$), 128.3 (s, *m*-Mes), 129.5 (d, $^4J_{PC}$ = 2.2 Hz, *p*-PPh$_3$), 131.3 (d, $^2J_{PC}$ = 3.5 Hz, *o*-Mes), 134.4 (s, *p*-Mes), 135.7 (d, $^2J_{PC}$ = 10.6 Hz, *o*-PPh$_3$), 136.4 (d, $^1J_{PC}$ = 51.9 Hz, *i*-PPh$_3$), 164.1 (dd, $^1J_{PC}$ = 90.3 Hz, $^3J_{PC}$ = 16.9 Hz, *i*-Mes). HRMS: calcd for $C_{37}H_{41}P_2Ir$ 740.23126; found 740.23122.

[Cp*(PH$_2$Mes*)Ir=PMes*] (8). 8 was prepared from **5a** (135 mg, 0.20 mmol), DBU (59.8 μL, 0.40 mmol), and Mes*PH$_2$ (55.6 mg, 0.20 mmol) as a dark purple powder (150 mg, 0.170 mmol, 85%). The compound could not be recrystallized properly due to high solubility and therefore contains minor impurities. ^{31}P NMR (C_6D_6): δ 714.7 (d, $^2J_{PP}$ = 20 Hz, Ir=P), −84.4 (dt, $^1J_{PH}$ = 384 Hz, $^2J_{PP}$ = 20 Hz, Ir−PH$_2$Mes*). ^{1}H NMR (C_6D_6): δ 1.27 (s, 9H, *p*-C(CH_3)$_3$), 1.42 (s, 9H, *p*-C(CH_3)$_3$), 1.48 (s, 18H, *o*-C(CH_3)$_3$), 1.66 (s, 15H, C$_5$(CH_3)$_5$), 1.70 (s, 18H, *o*-C(CH_3)$_3$), 6.68 (dd, 2H, $^1J_{PH}$ = 384 Hz, $^3J_{PH}$ = 8.2 Hz, PH_2), 7.45 (d, 2H, $^4J_{PH}$ = 2.1 Hz, *m*-Mes*), 7.56 (bs, 2H, *m*-Mes*). ^{13}C{^{1}H} NMR (C_6D_6): δ 9.94 (s, C$_5$(*C*H$_3$)$_5$), 31.5 (s, *p*-C(*C*H$_3$)$_3$), 32.0 (s, *p*-C(*C*H$_3$)$_3$), 32.4 (d, $^4J_{PC}$ = 7.0 Hz, *o*-C(*C*H$_3$)$_3$), 33.6 (d, $^4J_{PC}$ = 2.7 Hz, *o*-C(*C*H$_3$)$_3$), 34.6 (s, *p*-*C*(CH$_3$)$_3$), 34.8 (s, *p*-*C*(CH$_3$)$_3$), 38.5 (d, $^3J_{PC}$ = 0.9 Hz, *o*-*C*(CH$_3$)$_3$), 39.1 (s, *o*-*C*(CH$_3$)$_3$), 94.2 (d, $^2J_{PC}$ = 3.3 Hz, *C*$_5$(CH$_3$)$_5$), 120.4 (s, *m*-Mes*PH$_2$), 122.0 (d, $^3J_{PC}$ = 8.6 Hz, *m*-Mes*P=Ir), 125.6 (d, $^1J_{PC}$ = 36.5 Hz, *i*-Mes*PH$_2$), 145.7 (s, *o*-Mes*), 146.2 (s, *o*-Mes*), 149.7 (d, $^4J_{PC}$ = 2.4 Hz, *p*-Mes*), 153.9 (d, $^2J_{PC}$ = 4.9 Hz, *o*-Mes*), 169.1 (d, $^1J_{PC}$ = 99.2 Hz, *i*-Mes*P=Ir). HRMS: calcd for $C_{46}H_{75}P_2Ir$ 882.49725; found 882.49653.

[Cp*(PMe$_3$)Ir=PMes*] (9). 9 was prepared from **5a** (135 mg, 0.20 mmol), DBU (59.8 μL, 0.40 mmol), and PMe_3 (0.20 mL of a 1.0 M solution in toluene, 0.20 mmol) as a mixture of two isomers obtained as a dark purple-red powder (116 mg, 0.171 mmol, 85%). Major isomer (92%) (*E*)-**9**. ^{31}P NMR (C_6D_6): δ 629.3 (d, $^2J_{PP}$ = 83.5 Hz, Ir=P), −37.3 (d, $^2J_{PP}$ = 83.5 Hz, PMe$_3$). ^{1}H NMR (C_6D_6): δ 1.50 (s, 9H, *p*-C(CH_3)$_3$), 1.56 (s, 15H, C$_5$(CH_3)$_5$), 1.61 (d, $^2J_{PH}$ = 9.5 Hz, 9H, PMe$_3$), 1.75 (s, 18H, *o*-C(CH_3)$_3$), 7.48 (s, 2H, *m*-Mes*). ^{13}C{^{1}H} NMR (C_6D_6): δ 10.5 (s, C$_5$(*C*H$_3$)$_5$), 20.6 (dd, $^1J_{PC}$ = 38.1 Hz, $^3J_{PC}$ = 13.5 Hz, PMe$_3$), 32.2 (s, *p*-C(*C*H$_3$)$_3$), 32.5 (d, $^4J_{PC}$ = 8.9 Hz, *o*-C(*C*H$_3$)$_3$), 34.7 (s, *p*-*C*(CH$_3$)$_3$), 38.7 (s, *o*-*C*(CH$_3$)$_3$), 93.0 (d, $^2J_{PC}$ = 3.7 Hz, *C*$_5$(CH$_3$)$_5$), 120.4 (s, *m*-Mes*), 145.6 (s, *p*-Mes*), 145.7 (s, *o*-Mes*), 169.6 (dd, $^1J_{PC}$ = 108.4 Hz, $^3J_{PC}$ = 19.2 Hz, *i*-Mes*). HRMS: calcd for $C_{31}H_{53}P_2Ir$ 680.32513; found 680.32644. Minor isomer (8%) (*Z*)-**9**. ^{31}P NMR (C_6D_6): 726.6 (d, $^2J_{PP}$ = 17.6 Hz, Ir=P), −41.7 (d, $^2J_{PP}$ = 17.6 Hz, Ir−PMe$_3$). ^{1}H NMR (C_6D_6): δ 0.95 (d, $^2J_{PH}$ = 9.4 Hz, 9H, PMe$_3$), 1.46 (s, 9H, *p*-C(CH_3)$_3$), 1.64 (s, 18H, *o*-C(CH_3)$_3$), 1.99 (bs, 15H, C$_5$(CH_3)$_5$), 7.45 (s, 2H, *m*-Mes*).

[Cp*(P(OMe)$_3$)Ir=PMes*] (10). 10 was prepared from **5a** (135 mg, 0.20 mmol), DBU (59.8 μL, 0.40 mmol), and P(OMe)$_3$ (24 μL, 0.20 mmol) as a mixture of two isomers of **10** (136 mg, 0.187 mmol, 94%) obtained as dark purple-red crystals. Major isomer (96%) (*Z*)-**10**. ^{31}P NMR (C_6D_6): δ 797.0 (d, $^2J_{PP}$ = 8.8 Hz, Ir=P), 101.6 (d, $^2J_{PP}$ = 8.8 Hz, P(OCH$_3$)$_3$). ^{1}H NMR (C_6D_6): δ 1.43 (s, 9H, *p*-C(CH_3)$_3$), 1.61 (s, 18H, *o*-C(CH_3)$_3$), 2.02 (d, $^4J_{PH}$ = 2.1 Hz, 15H, C$_5$(CH_3)$_5$), 3.05 (d, $^3J_{PH}$ = 11.9 Hz, 9H, P(OCH_3)$_3$), 7.46 (s, 2H, *m*-Mes*). ^{13}C{^{1}H} NMR (C_6D_6): δ 10.1 (s, C$_5$(*C*H$_3$)$_5$), 31.9 (s, *p*-C(*C*H$_3$)$_3$), 32.6 (d, $^4J_{PC}$ = 7.2 Hz, *o*-C(*C*H$_3$)$_3$), 34.8 (s, *p*-*C*(CH$_3$)$_3$), 39.1 (s, *o*-*C*(CH$_3$)$_3$), 50.9 (d, $^2J_{PC}$ = 4.1 Hz, P(O*C*H$_3$)$_3$), 96.6 (d, $^2J_{PC}$ = 4.8 Hz, *C*$_5$(CH$_3$)$_5$), 120.9 (s, *m*-Mes*), 145.0 (s, *o*-Mes*), 146.4 (s, *p*-Mes*), 168.9 (dd, $^1J_{PC}$ = 102 Hz, $^3J_{PC}$ = 3 Hz, *i*-Mes*). HRMS: calcd for $C_{31}H_{53}O_3P_2Ir$ 728.30988; found 728.30834. Minor isomer (4%) (*E*)-**10**. ^{31}P NMR (C_6D_6): 680.3 (d, $^2J_{PP}$ = 20.4 Hz, Ir=P), 105.6 (d, $^2J_{PP}$ = 20.4 Hz, Ir−P(OCH$_3$)$_3$).

[(Cp*Ir=PMes*)$_2$dppe] (11). 11 was prepared from **5a** (135 mg, 0.20 mmol), DBU (59.8 μL, 0.40 mmol), and dppe (39.8 mg, 0.10 mmol) as dark red crystals (132 mg, 0.082 mmol, 82%). Mp: >205 °C (dec). ^{31}P NMR (C_6D_6): δ 654.8 (d, $^2J_{PP}$ = 69 Hz, Ir=P), 10.1 (d, $^2J_{PP}$ = 69 Hz, dppe). ^{1}H NMR (C_6D_6): δ 1.26 (s, 30H, C$_5$(CH_3)$_5$), 1.53 (s, 18H, *p*-C(CH_3)$_3$), 1.71 (s, 36H, *o*-C(CH_3)$_3$), 3.31 (bs, 4H, CH_2), 7.04−7.10 (m, 4H, *p*-PPh$_2$), 7.17−7.25 (m, 8H, *o*-PPh$_2$), 7.52 (s, 2H, *m*-Mes*), 7.85−7.93 (m, 8H, *m*-PPh$_2$). ^{13}C{^{1}H} NMR (C_6D_6): δ 9.63 (s, C$_5$(*C*H$_3$)$_5$), 23.7 (dd, $^1J_{PC}$ = 31.1 Hz, $^3J_{PC}$ = 21.2 Hz, *C*H$_2$), 32.3 (s, *o*-C(*C*H$_3$)$_3$), 32.5 (s, *p*-C(*C*H$_3$)$_3$), 34.7 (s, *p*-*C*(CH$_3$)$_3$), 38.7 (s, *o*-*C*(CH$_3$)$_3$), 93.6 (m, *C*$_5$(CH$_3$)$_5$), 120.6 (s, *m*-Mes*), 127.8 (s, *m*-PPh$_2$), 129.5 (s, *p*-PPh$_2$), 134.4 (m, *o*-PPh$_2$), 135.9 (d, $^1J_{PC}$ = 48.4 Hz, *i*-PPh$_2$), 145.2 (s, *o*-Mes*), 145.8 (s, *p*-Mes*), 170.1 (dd, $^1J_{PC}$ = 105.3 Hz, $^3J_{PC}$ = 15.6 Hz, *i*-Mes*). Anal. Calcd for $C_{82}H_{112}P_4Ir_2$: C, 61.32; H, 7.03; P, 7.71. Found: C, 60.23; H, 7.03; P, 7.46. HRMS could not be obtained due to the high molecular weight of the compound (1606.12). Performing the reaction with 1.2 equiv of dppe resulted in a 2:3 mixture of **11** and the mononuclear compound, [Cp*(dppe)Ir=PMes*]. ^{31}P NMR (C_6D_6): δ 655.9 (d, $^2J_{PP}$ = 83 Hz, Ir=*P*), 14.8 (dd, $^2J_{PP}$ = 83 Hz, $^3J_{PP}$ = 40 Hz, Ir−*P*Ph$_2$−CH$_2$CH$_2$PPh$_2$), −9.0 (d, $^3J_{PP}$ = 40 Hz, Ir−PPh$_2$−CH$_2$CH$_2$*P*Ph$_2$).

[Cp*(AsPh$_3$)Ir=PMes*] (12). 12 was prepared from **5a** (135 mg, 0.20 mmol), DBU (59.8 μL, 0.40 mmol), and $AsPh_3$ (61.2 mg, 0.20 mmol) as dark orange-red crystals (169 mg, 0.186 mmol, 93%). Mp: 173−174 °C. ^{31}P NMR (C_6D_6): δ 654.9 (s, Ir=P). ^{1}H NMR (C_6D_6): δ 1.40 (s, 15H, C$_5$(CH_3)$_5$), 1.51 (s, 9H, *p*-C(CH_3)$_3$), 1.66 (s, 18H, *o*-C(CH_3)$_3$), 7.06−7.22 (m, 9H, AsPh$_3$), 7.47 (s, 2H, *m*-Mes*), 7.89−7.93 (m, 6H, AsPh$_3$). ^{13}C{^{1}H} NMR (C_6D_6): δ 9.98 (s, C$_5$(*C*H$_3$)$_5$), 32.2 (s, *p*-C(*C*H$_3$)$_3$), 32.4 (d, $^4J_{PC}$ = 7.1 Hz, *o*-C(*C*H$_3$)$_3$), 34.6 (s, *p*-*C*(CH$_3$)$_3$), 38.6 (s, *o*-*C*(CH$_3$)$_3$), 91.4 (s, *C*$_5$(CH$_3$)$_5$), 120.4 (s, *m*-Mes*), 128.1 (s, *m*-AsPh$_3$), 129.4 (s, *p*-AsPh$_3$), 134.9 (s, *o*-AsPh$_3$), 137.3 (d, $^3J_{PC}$ = 3.1 Hz, *i*-AsPh$_3$), 145.9 (s, *o*-Mes*), 146.0 (s, *p*-Mes*), 168.9 (d, $^1J_{PC}$ = 112 Hz, *i*-Mes*). HRMS: calcd for $C_{46}H_{59}AsPIr$ 910.31989; found 910.32009.

[Cp*(*t*-BuNC)Ir=PMes*] (13). 13 was prepared from **5a** (135 mg, 0.20 mmol), DBU (59.8 μL, 0.40 mmol), and *t*-BuNC (23 μL, 0.20 mmol) as large dark pink-red crystals (125 mg, 0.182 mmol, 91%). Mp: 144−146 °C. ^{31}P NMR (C_6D_6): δ 740.1

(s, Ir=P). ^{1}H NMR (C_6D_6): δ 0.94 (s, 9H, CN−C(CH_3)$_3$), 1.44 (s, 9H, *p*-C(CH_3)$_3$), 1.69 (s, 18H, *o*-C(CH_3)$_3$), 2.09 (s, 15H, C_5(CH_3)$_5$), 7.52 (s, 2H, *m*-Mes*). ^{13}C{^{1}H} NMR (C_6D_6): δ 10.0 (s, C_5(*C*H$_3$)$_5$), 31.5 (s, C(*C*H$_3$)$_3$), 32.1 (s, C(*C*H$_3$)$_3$), 32.1 (d, $^4J_{PC}$ = 7.5 Hz, *o*-C(*C*H$_3$)$_3$), 34.9 (s, *p*-*C*(CH$_3$)$_3$), 39.1 (s, *o*-*C*(CH$_3$)$_3$), 55.3 (s, N*C*(CH$_3$)$_3$), 95.4 (s, C_5(CH$_3$)$_5$), 121.5 (s, *m*-Mes*), 142.9 (bs, *C*N), 145.4 (s, *p*-Mes*), 146.3 (s, *o*-Mes*), 167.6 (d, $^1J_{PC}$ = 97.2 Hz, *i*-Mes*). IR (KBr, cm^{-1}): ν(CN) 2120, 2076. HRMS: calcd for $C_{33}H_{53}NPIr$ 687.35443; found 687.35474.

[Cp*(XyNC)Ir=PMes*] (14). 14 was prepared from **5a** (135 mg, 0.20 mmol), DBU (59.8 μL, 0.40 mmol), and XyNC (26.3 mg, 0.20 mmol) as large dark pink-red crystals (137 mg, 0.186 mmol, 93%). Mp: 151−154 °C. ^{31}P NMR (C_6D_6): δ 757.1 (s, Ir=P). ^{1}H NMR (C_6D_6): δ 1.18 (s, 9H, *p*-C(CH_3)$_3$), 1.66 (s, 18H, *o*-C(CH_3)$_3$), 2.05 (s, 15H, C_5(CH_3)$_5$), 2.14 (s, 6H, XyCH_3), 6.76 (s, 3H, *m*,*p*-Xy), 7.33(s, 2H, *m*-Mes*). ^{13}C{^{1}H} NMR (C_6D_6): δ 10.1 (s, C_5(*C*H$_3$)$_5$), 19.5 (s, Xy*C*H$_3$), 31.7 (s, *p*-C(*C*H$_3$)$_3$), 32.6 (d, $^4J_{PC}$ = 6.9 Hz, *o*-C(*C*H$_3$)$_3$), 34.5 (s, *p*-*C*(CH$_3$)$_3$), 38.8 (s, *o*-*C*(CH$_3$)$_3$), 96.7 (s, C_5(CH$_3$)$_5$), 120.9 (s, *m*-Mes*), 125.9 (s, *p*-Xy), 127.7 (s, *m*-Xy), 131.2 (bs, *i*-Xy), 134.7 (s, *o*-Xy), 145.2 (s, *p*-Mes*), 146.9 (s, *o*-Mes*), 154.6 (bs, CN), 166.8 (d, $^1J_{PC}$ = 93.7 Hz, *i*-Mes*). IR (KBr, cm^{-1}): ν(CN) 2064, 2023. HRMS: calcd for $C_{37}H_{53}NPIr$ 735.35443; found 735.35360.

[Cp*(CO)Ir=PMes*] (15). 15 was prepared from **5a** (250 mg, 0.37 mmol), DBU (112 μL, 0.75 mmol), and carbon monoxide (which was passed through the reaction mixture) as deep red crystals (205 mg, 0.325 mmol, 88%). Mp: 156−157 °C. ^{31}P NMR (C_6D_6): δ 804.6 (s, Ir=P). ^{1}H NMR (C_6D_6): δ 1.43 (s, 9H, *p*-C(CH_3)$_3$), 1.56 (s, 18H, *o*-C(CH_3)$_3$), 1.90 (s, 15H, C_5(CH_3)$_5$), 7.49 (s, 2H, *m*-Mes*). ^{13}C{^{1}H} NMR (C_6D_6): δ 9.75 (s, C_5(*C*H$_3$)$_5$), 31.9 (s, *p*-C(*C*H$_3$)$_3$), 32.6 (d, $^4J_{PC}$ = 7.3 Hz, *o*-C(*C*H$_3$)$_3$), 34.8 (s, *p*-*C*(CH$_3$)$_3$), 38.5 (s, *o*-*C*(CH$_3$)$_3$), 99.0 (s, C_5(CH$_3$)$_5$), 121.2 (s, *m*-Mes*), 145.0 (s, *o*-Mes*), 148.8 (s, *p*-Mes*), 164.5 (d, $^1J_{PC}$ = 89.4 Hz, *i*-Mes*), 179.0 (s, CO). IR (KBr, cm^{-1}): ν(CO) 1968 (s). HRMS: calcd for $C_{29}H_{44}OPIr$ 632.27588; found 632.27560.

Reaction of 15 with CH_2I_2 and CHI_3 on NMR Scale. A small excess of CH_2I_2 (0.12 mmol) was added to a dark red solution of **15** (0.10 mmol) in *n*-pentane (0.5 mL). The orange-red precipitate of Cp*(CO)IrI_2, formed quantitatively over a period of 48 h at room temperature, was removed by decanting the solution and washing the residue twice with *n*-pentane (1 mL). The combined *n*-pentane solutions were evaporated to yield **16** as a yellow solid (**16**). Performing the reaction with CHI_3 resulted in the formation of orange-colored **17**.

Cp*(CO)IrI_2: ^{1}H NMR ($CDCl_3$): δ 2.20 (s, 15H, C_5(CH_3)$_5$). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 10.8 (s, C_5(*C*H$_3$)$_5$), 100.2 (s, C_5(CH$_3$)$_5$), 164.1 (s, *C*O). IR (KBr, cm^{-1}): ν(CO) 2018 (s). **16**: ^{31}P NMR ($CDCl_3$): δ 289.7 (t, $^2J_{PH}$ = 30.4 Hz). ^{1}H and ^{13}C NMR were as reported in the literature.[22] **17**: ^{31}P NMR ($CDCl_3$): δ 310.2 (d, $^2J_{PH}$ = 39.7 Hz, (*Z*)-**17**, 73%), 293.1 (d, $^2J_{PH}$ = 26.4 Hz, (*E*)-**17**, 27%). ^{1}H and ^{13}C NMR are as reported in the literature.[23]

Crystal Structure Determination of Complexes 3 and 15. X-ray intensities were measured on a Nonius KappaCCD diffractometer with rotating anode (λ = 0.71073 Å). The structures were solved with automated Patterson methods (DIRDIF97)[28] and refined with SHELXL97[29] against F^2 of all reflections. Molecular illustration, structure checking, and calculations were performed with the PLATON package.[30]

Crystal Structure Determination of 3. $C_{46}H_{59}IrP_2$, M_r = 866.07, black block, 0.27 × 0.20 × 0.11 mm^3, temp = 150(2) K, triclinic, space group $P\bar{1}$ (No. 2), a = 9.7474(1) Å, b = 14.4034(2) Å, c = 16.9057(2) Å, α = 64.8313(5)°, β = 78.2842(5)°, γ = 72.4545(5)°, V = 2040.49(4) Å^3, Z = 2, ρ = 1.410 g/cm^3. Absorption correction based on multiple measured reflections (PLATON,[30] routine MULABS, μ = 3.38 mm^{-1}, 0.54−0.71 transmission); 51 672 measured reflections up to (sin $\theta/\lambda)_{max}$ = 0.65 Å^{-1}, of which 9232 were unique (R_{int} = 0.0491). R [$I > 2\sigma(I)$]: R1 = 0.0200, wR2 = 0.0475. R [all reflections]: R1 = 0.0219, wR2 = 0.0484. S = 1.061.

Crystal Structure Determination of 15. $C_{29}H_{44}IrOP$, M_r = 631.81, dark red plate, 0.24 × 0.24 × 0.09 mm^3, temp = 130(2) K, orthorhombic, space group *Pnma* (No. 62), a = 18.0642(1) Å, b = 14.7379(1) Å, c = 10.5269(1) Å, V = 2802.56(4) Å^3, Z = 4, ρ = 1.497 g/cm^3. Analytical absorption correction (PLATON,[30] routine ABST, μ = 4.84 mm^{-1}, 0.32−0.53 transmission); 75 667 measured reflections up to (sin $\theta/\lambda)_{max}$ = 0.90 Å^{-1}, of which 8861 were unique (R_{int} = 0.0490). R [$I > 2\sigma(I)$]: R1 = 0.0287, wR2 = 0.0742. R [all reflections]: R1 = 0.0485, wR2 = 0.0815. S = 0.891.

Acknowledgment. This work was supported by The Netherlands Foundation for Chemical Sciences (CW) with financial aid from The Netherlands Organization for Scientific Research (NWO). Dr. H. Zappey is acknowledged for measuring high-resolution mass spectra.

Supporting Information Available: ^{1}H NMR spectra of compounds **3**, **5a**−**c**, and **6**−**15**. Crystallographic data for compounds **3** and **15**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM020062T

(28) 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.

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

(30) Spek, A. L. *PLATON*, a multipurpose crystallographic tool; Utrecht University: The Netherlands, 2001.