Calcd for $C_{33}H_{42}IrOP$: C, 58.46; H, 6.26. Found: C, 58.75; H, 6.45.

c, X = MeO: mp 75–80 °C dec; ^1H NMR (C_6D_6) δ 7.84–7.77 (m, 6 H), 6.80–6.76 (m, 6 H), 3.92–3.67 (dm, 2 H), 3.23 (9 H), 1.67 (d, J = 2.0 Hz, 15 H), 1.22 (t, J = 6.7 Hz, 3 H), −13.31 (d, J = 37.9 Hz, 1 H); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 161.0 ($C_6H_4OCH_3$), 135.9 (d, J = 11.8 Hz, ortho or meta PC_6H_4), 127.8 (d, J_{PC} = 58.4 Hz, ipso PC, obscured by solvent), 113.3 (d, J = 11.0 Hz, ortho or meta PC_6H_4), 91.3 (d, J = 3.4 Hz, C_5Me_5), 75.8 (OCH_2CH_3), 54.7 ($C_6H_4OCH_3$), 24.2 (OCH_2CH_3), 9.9 (C_5Me_5); $^{31}P\{^1H\}$ NMR (C_6D_6) δ 9.7; IR (KBr) 2063, 1595, 1500, 1099 cm^{-1}. Anal. Calcd for $C_{33}H_{42}IrO_4P$: C, 54.60; H, 5.84. Found: C, 54.96; H, 6.06.

Cp*Ir(PAr$_3$)PPh$_3$ (Ar = p-XC$_6$H$_4$; X = F, Me, MeO) (21a–c). These compounds were prepared from **3** and the appropriate triarylphosphine as with the synthesis of **17**. Like **17** they are red crystalline solids.

a, X = F: mp 180–190 °C; ^1H NMR (C_6D_6) δ 7.65–7.40 (m), 6.90 (m), 6.63 (m), 1.47 (d, J = 1.2 Hz, 15 H); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 163.2 (d, J_{CF} = 249 Hz, CF), 139.1 (d, J = 47.8 Hz, ipso PC), 136.7 (m), 135.1 (d, J = 11.4 Hz), 134.6, 126.8 (d, J = 9.7 Hz), 113.6 (m), 93.2 (C_5Me_5), 10.6 (C_5Me_5); $^{31}P\{^1H\}$ NMR (C_6D_6) δ 20.4 (d, J = 21.9 Hz, PPh_3), 16.7 (d, J = 23 Hz, PAr_3); $^{31}P\{^1H\}$ NMR (toluene-d_8) δ 20.5 (d, J = 21.5 Hz), 16.6 (d, J = 21.5 Hz); IR (KBr) 1230, 1195, 1161, 1118, 1094 cm^{-1}. Anal. Calcd for $C_{46}H_{42}IrP_2F_3$: C, 60.98; H, 4.68. Found: C, 60.95; H, 4.70. FAB-MS (sulfolane): m/e 907/905, $(MH)^+$.

b, X = Me: mp 120 °C; ^1H NMR (C_6D_6) δ 7.8–7.6 (m), 7.0–6.9 (m), 6.80 (m), 2.04 (9 H), 1.62 (15 H); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 140.1, 139.4, 137.6, 137.0, 136.4, 135.4 (d, J = 11.3 Hz), 127.5, 127.4 (obscured by solvent), 126.6 (d, J = 9.5 Hz), 93.0 (C_5Me_5), 21.1 ($C_6H_4CH_3$), 10.8 (C_5Me_5); $^{31}P\{^1H\}$ NMR (C_6D_6) δ 20.5 (d, J = 22.4 Hz), 17.3 (d, J = 22.4 Hz); $^{31}P\{^1H\}$ NMR (toluene-d_8) δ 20.5 (d, J = 22.5 Hz), 17.2 (d, J = 22.5 Hz); IR (KBr) 1192, 1118, 1094 cm^{-1}. Anal. Calcd for $C_{49}H_{51}IrP_2$: C, 65.82; H, 5.76. Found: C, 65.38; H, 5.76. FAB-MS (sulfolane): m/e 895/893, $(MH)^+$ ($^{193}Ir/^{191}Ir$).

c, X = MeO: ^1H NMR (C_6D_6) δ 7.74 (m), 7.1–6.9 (m), 6.64 (m), 3.27 (9 H), 1.63 (15 H); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 159.0 ($COMe$), 139.8 (d, J = 46.8 Hz), 136.6 (d, J = 12.6 Hz), 135.3 (d, J = 11.2 Hz), 131.6 (d, J = 51.8 Hz), 126.6 (d, J = 9.6 Hz), 112.2 (d, J = 10.5 Hz), 93.0 (C_5Me_5), 54.7 ($C_6H_4OCH_3$), 10.9 (C_5Me_5); $^{31}P\{^1H\}$ NMR (C_6D_6) δ 21.0 (d, J = 22.5 Hz), 14.6 (d, J = 22.1 Hz); $^{31}P\{^1H\}$ NMR (toluene-d_8) δ 21.0 (d, J = 22.5 Hz), 14.6 (d, J = 22.5 Hz); IR (KBr) 1255, 1181, 1120, 1097 cm^{-1}. Anal. Calcd for $C_{49}H_{51}IrP_2O_3$: C, 62.46; H, 5.47. Found: C, 62.36; H, 5.62. FAB-MS (sulfolane): m/e 943/941, $(MH)^+$ ($^{193}Ir/^{191}Ir$).

Cp*Ir(PPh$_2$Me)$_2$ (22). A flask was charged with Cp*Ir(PPh$_2$Me)Cl$_2$ (338 mg, 0.565 mmol), NaOEt (102 mg, 1.50 mmol), and a stir bar. Ethanol (20 mL) was condensed into the flask and thawed. After 1.5 h of stirring, the orange slurry had turned yellow. The ethanol was removed in vacuo to given an orange oil. The oil was extracted with hexane, filtered to remove NaCl and excess NaOEt, concentrated, and cooled to −40 °C to give an orange oil, presumably Cp*Ir(PPh$_2$Me)(OEt)(H). To 293 mg (0.51 mmol) of this material in 10 mL of hexane was added PPh$_2$Me (105 mg, 0.525 mmol) in 5 mL of hexane. After 5 h the solvent was removed in vacuo from the orange solution to give a red oil. Trituration of this oil at ambient temperature with hexamethyldisiloxane left a red powder. Additional crops were obtained by concentration of the hexamethyldisiloxane solution for a total yield of 248 mg (67%): ^1H NMR (C_6D_6) δ 7.73–7.67 (m, 8 H), 7.18–7.03 (m, 12 H), 1.75 (d, J = 7.5 Hz), 1.69 (broad, 15 H); $^{31}P\{^1H\}$ NMR (C_6D_6) δ −5.5; $^{13}C\{^1H\}$ NMR (C_6D_6) δ 142.1–141.2 (5-line pattern, ipso PPh), 133.3 (broad), 128.3 (partially obscured by C_6D_6), 127.3 (broad), 92.3 (C_5Me_5), 23.2–22.4 (5-line pattern, PMe), 10.8 (C_5Me_5); IR (KBr) 3053, 2916, 1435, 1098, 879, 797, 513 cm^{-1}. Anal. Calcd for $C_{36}H_{41}IrP_2$: C, 59.40; H, 5.69. Found: C, 56.03; H, 5.49. Correct analysis for C could not be obtained even on red crystals formed on multiple recrystallization from pentane.

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Supplementary Material Available: Tables of positional parameters and temperature factors for **6c** (4 pages); a listing of X-ray structural details for **6c** (20 pages). Ordering information is given on any current masthead page.

Mechanism of Ligand Substitution in an Iridium Amide Complex

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Reaction of Cp*IrPPh$_3$Cl$_2$ (Cp* = η^5-C$_5$Me$_5$) with methyllithium gave Cp*IrPPh$_3$Me$_2$ (**1a**), which yielded Cp*IrPPh$_3$(Me)(Cl) (**2a**) on treatment with anilinium hydrochloride. The reactions of complex **2a** with silver acetate, benzylmagnesium chloride, and lithium anilide gave Cp*IrPPh$_3$(Me)(OAc) (**3a**), Cp*IrPPh$_3$(Me)(CH$_2$Ph) (**4a**), and Cp*IrPPh$_3$(Me)(NHPh) (**5a**), respectively. Cp*IrPPh$_3$(Me)(OPh) (**6a**) was prepared from **2a** and sodium phenoxide or from **3a** and potassium phenoxide. Reaction of **2a** with sodium ethoxide in ethanol gave Cp*IrPPh$_3$(Me)(H) (**7a**). Treatment of **1a–6a** with PPh$_2$Me gave PPh$_3$ and the corresponding Cp*Ir(PPh$_2$Me)(Me)(X) compounds (X = Me, **1b**; X = Cl, **2b**; X = OAc, **3b**; X = CH$_2$Ph, **4b**; X = NHPh, **5b**; X = OPh, **6b**). Complexes **1b–6b** were prepared independently as for **1a–6a** via Cp*Ir(PPh$_2$Me)Cl$_2$. The rate of the reaction of **5a** and PPh$_2$Me to give PPh$_3$ and **5b** does not depend on [PPh$_2$Me]. On the basis of this result, the temperature dependence of the rate, and the lack of inhibition by PPh$_3$, **5a** is proposed to reversibly form the ring-slipped intermediate (η^3-C$_5$Me$_5$)IrPPh$_3$(Me)(NHPh) (**8**), which is stabilized by nitrogen lone pair to metal electron donation and trapped by PPh$_2$Me to give the observed products. The large rate differences in the ligand substitutions of **1a–6a** are rationalized in light of this mechanism.

Introduction

Until recently, alkoxide and amide complexes of the late transition metals were uncommon, and the properties of M–O and M–N bonds in such compounds were little investigated.[1] The reactivity of these bonds often depends dramatically on the other ligands in the coordination sphere of the metal complex. In the iridium alkoxide and

(1) For a review see: Bryndza, H. E.; Tam, W. *Chem. Rev.* **1988**, *88*, 1163.

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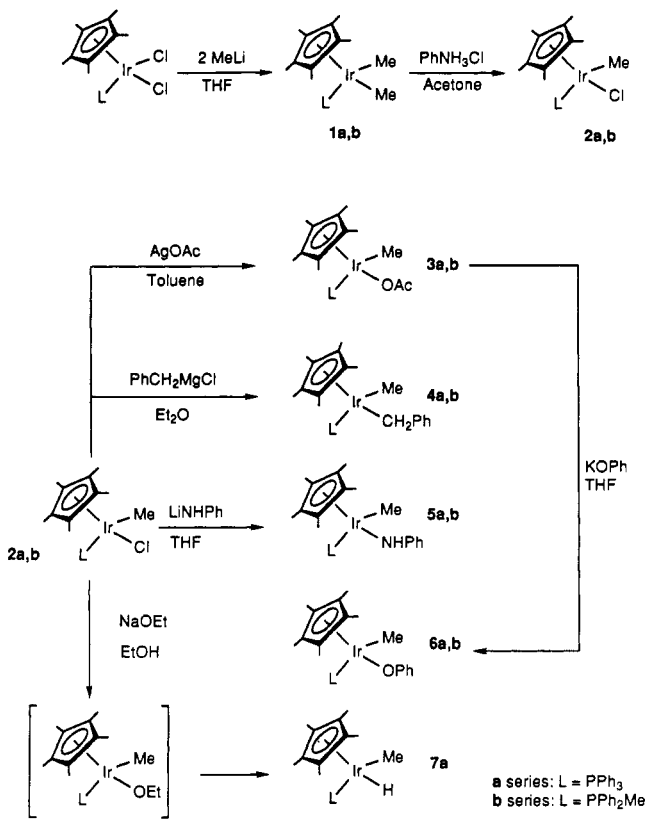
Scheme I



amide complexes $Cp^*IrPPh_3(H)(X)$, where X = OR or NHR, for example, elimination of alcohol or amine induced by an entering ligand is often observed.[2] To examine the properties of Ir–O and Ir–N bonds in the absence of the hydride ligand, we have prepared the methyl complexes $Cp^*IrPPh_3(Me)(X)$, where X = OPh or NHPh, for comparison with the corresponding hydrides $Cp^*IrPPh_3(H)(X)$. The methyl compounds readily undergo substitution of the triphenylphosphine, which is not observed in the hydride series. The rate of this process is strongly dependent on the nature of X, demonstrating that alkoxides and amides can affect the reactivity of a metal complex even when reaction does not occur at the metal–heteroatom bond.

Results and Discussion

Preparation of Methyl Compounds $Cp^*IrPPh_3(Me)(X)$. As summarized in Scheme I, treatment of $Cp^*IrPPh_3Cl_2$ with 2 equiv of methyllithium in THF gave $Cp^*IrPPh_3Me_2$ (**1a**, 69% yield), which was selectively chlorinated with anilinium hydrochloride in acetone to form $Cp^*IrPPh_3(Me)(Cl)$ (**2a**, 72%), as previously observed for the trimethylphosphine analogues.[3] This methyl chloride complex undergoes straightforward metathesis reactions. Treatment of **2a** with silver acetate in toluene gave $Cp^*IrPPh_3(Me)(OAc)$ (**3a**, 67%) and with benzylmagnesium chloride in ether gave $Cp^*IrPPh_3(Me)(CH_2Ph)$ (**4a**, 49%). The anilide derivative $Cp^*IrPPh_3(Me)(NHPh)$ (**5a**, 80%) was prepared with lithium anilide in THF. The phenoxide $Cp^*IrPPh_3(Me)(OPh)$ (**6a**) may also be made from chloride **2a**, but is more conveniently prepared from acetate **3a** with potassium phenoxide in THF in 71% yield.

Reaction of methyl chloride complex **2a** with NaOEt in EtOH, however, did not yield the desired methyl ethoxide complex. Stirring **2a** with sodium ethoxide in ethanol at room temperature, conditions under which the hydrido ethoxide complex $Cp^*IrPPh_3(OEt)(H)$ is stable, gives the methyl hydride $Cp^*IrPPh_3(Me)(H)$ (**7a**) in 82% yield. Running the reaction at 0 °C in toluene/ethanol gives mixtures in which the desired ethoxide can be detected by ^1H NMR spectroscopy [characteristic diastereotopic ethoxide protons at δ 3.8–3.5 (C_6D_6) and signals due to Cp*, Me, and PPh_3] along with starting material **2a** and methyl

(2) Glueck, D. S.; Newman Winslow, L. J.; Bergman, R. G. *Organometallics*, preceding article in this issue.
(3) Buchanan, J. M.; Stryker, J. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 1537.

Table I. Rate Data for Reaction of 5a with PPh_2Me in Toluene at 10 °C

$[PPh_2Me]$, M	10^4k_{obs}, s^{-1}	$[PPh_3]$, M
6.88×10^{-2}	2.81	
5.05×10^{-2}	2.70	
3.79×10^{-2}	2.67	
1.38×10^{-2}	2.75	
5.52×10^{-3}	2.73	
4.60×10^{-3}	2.70	6.03×10^{-3}
3.60×10^{-3}	2.92	
3.60×10^{-3}	2.69	1.57×10^{-2}
3.07×10^{-3}	2.59	1.88×10^{-2}
6.90×10^{-4}	3.08	

Table II. Variable-Temperature Rate Data for Reaction of 5a with PPh_2Me in Toluene

T, K	k_{obs}, s^{-1}	T, K	k_{obs}, s^{-1}
273	8.38×10^{-5}	308	5.07×10^{-3}
283	2.81×10^{-4}	318	1.26×10^{-2}
293	1.17×10^{-3}	333	4.09×10^{-2}
298	1.74×10^{-3}		

Table III. ^1H NMR Data for $Cp^*IrPPh_3(Me)(X)$ Compounds[a]

compd	δ	mult	J, Hz	assgnt	integral
1a (X = Me)	7.52–7.46	m		PPh_3	6
	7.10–7.01	m		PPh_3	9
	1.41	d	1.6	C_5Me_5	15
	0.57	d	4.9	Ir*Me*	6
2a (X = Cl)	7.77–7.74	m		PPh_3	6
	7.0–6.9	m		PPh_3	9
	1.41	d	6.4	Ir*Me*	3
	1.24	d	1.5	C_5Me_5	15
3a (X = OAc)	7.70–7.64	m		PPh_3	6
	7.10–7.03	m		PPh_3	9
	1.83			OC(O)*Me*	3
	1.47	d	5.5	Ir*Me*	3
	1.39			C_5Me_5	15
4a (X = CH_2Ph)[b]	7.37	br m		PPh_3	15
	6.90	m		CH_2Ph	2
	6.79	m		CH_2Ph	1
	6.63	m		CH_2Ph	2
	2.99–2.48	dq		CH_2Ph	2
	1.27	d	1.5	C_5Me_5	15
	0.21	d	5.2	Ir*Me*	3
5a (X = NHPh)[c]	7.34–7.27	br m		PPh_3	15
	6.47–6.42	m		NH*Ph*	2
	5.88–5.86	m		NH*Ph*	2
	5.75–5.70	m		NH*Ph*	1
	1.50	d	1.7	C_5Me_5	15
	0.54	d	5.4	Ir*Me*	3
6a (X = OPh)[c]	7.55–7.53	m		PPh_3	6
	7.50–7.32	m		PPh_3	9
	6.69	t	7.7	O*Ph*	2
	6.19	d	8.2	O*Ph*	2
	6.10	t	7.0	O*Ph*	1
	1.38	d	1.5	C_5Me_5	15
	1.02	d	6.7	Ir*Me*	3
7a (X = H)	7.63–7.57	m		PPh_3	6
	7.06–7.00	m		PPh_3	9
	1.66	d	1.0	C_5Me_5	15
	0.72	d	5.0	Ir*Me*	3
	−16.73	d	35.1	Ir*H*	1

[a] All spectra in C_6D_6 at 20 °C unless indicated. [b] CD_2Cl_2. [c] THF-d_8.

Table IV. ^{1}H NMR Data for Cp*Ir(PPh$_2$Me)(Me)(X) Compounds[a]

compd	δ	mult	J, Hz	assgnt	integral
1b (X = Me)	7.34–7.28	m		P*Ph*$_2$Me	4
	7.10–7.02	m		P*Ph*$_2$Me	6
	1.69	d[b]	9.1	PPh$_2$*Me*	3
	1.44	d	1.4	C$_5$*Me*$_5$	15
	0.55	d	5.1	Ir*Me*	6
2b (X = Cl)[b]	7.59–7.41	m		P*Ph*$_2$Me	10 (tot)
	7.39	m		P*Ph*$_2$Me	
	1.97	d	10.0	PPh$_2$*Me*	3
	1.41	d	1.9	C$_5$*Me*$_5$	15
	0.77	d	6.2	Ir*Me*	3
3b (X = OAc)	7.8–7.7	m		P*Ph*$_2$Me	10 (tot)
	7.5–7.4	m		P*Ph*$_2$Me	
	7.1–7.0	m		P*Ph*$_2$Me	
	2.28			OC(O)*Me*	3
	1.89	d	10.0	PPh$_2$*Me*	3
	1.41	d	1.8	C$_5$*Me*$_5$	15
	1.13	d	5.9	Ir*Me*	3
4b (X = CH$_2$Ph)	7.46–7.41	m		CH$_2$*Ph*	2
	7.18	m		P*Ph*$_2$Me	10
	7.04–7.02	m		CH$_2$*Ph*	3
	3.0	m		C*H*$_2$Ph	2
	1.57	d	9.1	PPh$_2$*Me*	3
	1.33			C$_5$*Me*$_5$	15
	0.77	d	4.9	Ir*Me*	3
5b (X = NHPh)[b]	7.40–7.22	m		P*Ph*$_2$Me	10
	6.83	t	7.7	NH*Ph*	2
	6.19	d	8.0	NH*Ph*	2
	6.01	t	7.0	NH*Ph*	1
	1.74	d	9.6	PPh$_2$*Me*	3
	1.55	d	1.7	C$_5$*Me*$_5$	15
	1.37			N*H*	1
	0.30	d	5.7	Ir*Me*	3
6b (X = OPh)	7.55	t	8.9	O*Ph*	2
	7.33	m		P*Ph*	4
	7.08	m		P*Ph*	6
	6.90	d	8.0	O*Ph*	2
	6.74	t	7.0	O*Ph*	1
	1.77	d	10.3	P*Me*	3
	1.32	d	1.3	C$_5$*Me*$_5$	15
	1.27	d	6.6	Ir*Me*	3

[a] All spectra in C_6D_6 at 20 °C unless indicated. [b] CD_2Cl_2. [c] THF-d_8.

hydride **7**. However, we could not isolate this compound, which apparently undergoes rapid β-hydride elimination to give the observed hydride complex.

The iridium-bound methyl group in complexes **2a–7a** displays characteristic high-field resonances in both the proton and the carbon NMR spectra, as seen in Tables III and V. The acetate group in **3a** could be identified by its IR (ν_{CO} = 1625 cm^{-1}) and carbon NMR spectra (δ 177.6 for the carbonyl carbon). Benzyl, anilide, and phenoxide compounds **4a–6a** show three peaks in a 2:2:1 ratio in the ^{1}H NMR spectra, as expected for the phenyl resonances. The N–H stretch of the anilide **5a** appears at 3351 cm^{-1} in the IR spectrum. The benzylic protons of **4a** give rise to a complicated pattern at δ 2.99–2.48 in the ^{1}H NMR spectrum. The hydride ligand in **7** was identified by its ^{1}H NMR (δ −16.73, d, J_{PH} = 35.1 Hz) and IR (ν_{Ir-H} = 2097 cm^{-1}) absorptions.

Ligand Substitution Processes in Cp*IrPPh$_3$(Me)(X) Compounds. Reductive elimination of alcohol or amine from the hydrido alkoxide and amide compounds Cp*IrPPh$_3$(H)(X) (X = OEt, NHPh, NHCH$_2$Ph) induced by PPh$_3$ proceeds under mild conditions.[2] We hoped that the methyl analogues Cp*IrPPh$_3$(Me)(X) would provide an opportunity to directly compare O–H and N–H elimination with O–C and N–C eliminations. In no case, however, did we observe such an elimination of the Ir-bound methyl group. Treatment of the methyl complex Cp*IrPPh$_3$(Me)(NHPh) (**5a**) with PPh$_3$ did not give *N*-methylaniline; no reaction occurred up to 85 °C, at which temperature the Ir complex slowly decomposed. However, on reaction with tri-*p*-tolylphosphine, other substituted triarylphosphines, and trimethyl phosphite at room temperature, rapid phosphine exchange leading to an apparent equilibrium mixture was observed by ^{1}H and ^{31}P NMR spectroscopy, as shown in eq 1.

Table V. ^{13}C{^{1}H} NMR Data for Cp*IrPPh$_3$(Me)(X) Compounds[a]

compd	δ	mult	J, Hz	assgnt
1a (X = Me)	134.7	d	10.0	o or m P*Ph*$_3$
	134.5	d	49.3	ipso P*Ph*$_3$
	129.2			p
	127.6	d	9.7	o or m[d]
	92.4	d	3.3	*C*$_5$Me$_5$
	8.3			C$_5$*Me*$_5$
	−20.6	d	8.7	Ir*Me*
2a (X = Cl)	135.0	d	10.0	o or m
	134.0	d	52.1	ipso
	129.8			p
	127.8			*Ph*[d]
	92.8	d	3.1	*C*$_5$Me$_5$
	8.2			C$_5$*Me*$_5$
	−15.1	d	9.8	Ir*Me*
3a (X = OAc)	177.6			*C*O
	135.1	d	10.2	o or m
	133.4	d	51.8	ipso
	133.1			p
	127.9			*Ph*[d]
	91.4	d	3.1	*C*$_5$Me$_5$
	23.4			OC(O)*Me*
	8.8			C$_5$*Me*$_5$
	−9.9	d	10.4	Ir*Me*
4a (X = CH$_2$Ph)[b]	153.0	d	3.6	ipso *C*H$_2$Ph
	134.9	d	9.6	o or m P*Ph*$_3$
	133.6	d	49.5	ipso P*Ph*$_3$
	129.5			*Ph*
	128.5			*Ph*
	127.7	d	9.6	o or m P*Ph*$_3$
	126.9			CH$_2$*Ph*
	121.9			CH$_2$*Ph*
	93.3	d	3.4	*C*$_5$Me$_5$
	8.4			C$_5$*Me*$_5$
	−0.4	d	7.6	IrCH$_2$Ph
	−18.9	d	9.7	Ir*Me*
5a (X = NHPh)[b]	158.4			ipso N*C*$_6$H$_5$
	134.4	d	9.6	o or m P*Ph*$_3$
	133.5	d	49.4	ipso P*Ph*$_3$
	130.0			*Ph*
	127.91	d	9.0	o or m P*Ph*$_3$[e]
	127.90			*Ph*[e]
	116.7			*Ph*
	108.9			*Ph*
	93.1	d	3.1	*C*$_5$Me$_5$
	8.8			C$_5$*Me*$_5$
	−13.1	d	9.4	Ir*Me*
6a (X = OPh)[b]	167.7	d	2.8	ipso O*C*$_6$H$_5$
	134.7	d	9.8	o or m P*Ph*$_3$
	132.9	d	51.4	ipso P*Ph*$_3$
	130.0			*Ph*
	128.0			*Ph*[e]
	127.9	d	10.0	o or m P*Ph*$_3$[e]
	121.1			O*Ph*
	112.7			O*Ph*
	91.3	d	3.4	*C*$_5$Me$_5$
	9.0			C$_5$*Me*$_5$
	−10.9	d	9.9	Ir*Me*
7 (X = H)	136.6	d	51.8	ipso
	134.1	d	10.4	o or m
	129.2			p
	127.8			o or m[d]
	92.5	d	3.3	*C*$_5$Me$_5$
	9.5			C$_5$*Me*$_5$
	−32.7	d	7.3	Ir*Me*

[a] All spectra in C_6D_6 at 20 °C unless indicated. [b] CD_2Cl_2. [c] THF-d_8. [d] Partially obscured by C_6D_6. [e] Overlapping peaks.

$$[Ir]\text{-}PPh_3 + L \rightleftharpoons [Ir]\text{-}L + PPh_3$$
$$[Ir] = Cp^*Ir(Me)(NHPh) \qquad (1)$$
$$L = PAr_3,\ P(OMe)_3$$

Diphenylmethylphosphine cleanly substitutes triphenylphosphine at room temperature; the reaction goes to completion, within the limits of our detection by NMR spectroscopy, even if only 1 equiv of PPh_2Me is used. However, equilibrium can also be established in this case: addition of a large excess of PPh_3 to the isolated PPh_2Me complex regenerated a small amount of the triphenylphosphine compound. No such exchange is observed with the hydrido analogues $Cp^*IrPPh_3(OEt)(H)$ or $Cp^*IrPPh_3(NHPh)(H)$, which on reaction with PPh_2Me give $Cp^*IrPPh_3(PPh_2Me)$ and ethanol and aniline, respectively.[2]

Kinetic Studies. The kinetics of the substitution of PPh_2Me for PPh_3 in the anilido methyl complex $Cp^*IrPPh_3(Me)(NHPh)$ (**5a**) were investigated with UV–visible spectroscopy at 10 °C in toluene solution. Under the pseudo-first-order conditions of the experiment (PPh_2Me:Ir ratio greater than 10:1), the reverse reaction of the product with the liberated PPh_3 is slow. The reaction was monitored by observing the disappearance of a band due to starting material at 470 nm.[4] As shown in Table I and Figure 1, no rate dependence on PPh_2Me concentration was observed over the range from 6.88×10^{-2} to 6.90×10^{-4} M. This result is consistent with a mechanism involving reversible formation of an intermediate which is trapped by PPh_2Me more rapidly than it returns to **5a**.

The simplest explanation of this result is the dissociative mechanism shown in eq 2 involving reversible loss of PPh_3

$$\underset{\textbf{5a}}{Cp^*IrPPh_3(Me)(NHPh)} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Y + PPh_3 \xrightarrow{k_2[PPh_2Me]} Cp^*Ir(PPh_2Me)(Me)(NHPh) \qquad (2)$$

to give the intermediate $Cp^*Ir(Me)(NHPh)$, which is trapped by PPh_2Me to yield the observed products. This predicts the rate law shown in eq 3, which reduces to the

$$k_{obs} = \frac{k_1k_2[PPh_2Me]}{k_{-1}[PPh_3] + k_2[PPh_2Me]} \qquad (3)$$

$$\text{if } k_2[PPh_2Me] \gg k_{-1}[PPh_3] \text{ then } k_{obs} = k_1$$

simpler form $k_{obs} = k_1$, consistent with the observations. If this mechanism were operating, it is likely that addition of free PPh_3 would make the k_{-1} and k_2 steps competitive, resulting in rate inhibition by PPh_3. When the reaction was run under identical conditions in the presence of excess PPh_3, however, the rate was the same, within experimental error, as that observed without PPh_3. As shown in Table I and Figure 1, PPh_3:PPh_2Me ratios from 1.3:1 to 6.1:1 were used, corresponding to PPh_3:Ir ratios from 21:1 to 87:1, with a PPh_2Me:Ir ratio always greater than 10:1. At greater PPh_3:PPh_2Me ratios (PPh_3 concentrations greater than 2×10^{-2} M) plots of absorbance vs time no longer showed simple exponential behavior. We believe this is due to interference from the back-reaction of the product with PPh_3.

(4) Consistent results were obtained by observing the growth of a band due to product at 380 nm. Since the product $Cp^*Ir(PPh_2Me)(Me)(NHPh)$ reacts slowly with PPh_2Me under these conditions, all rates given above were obtained by analysis of the rate of disappearance of starting material. The error limits on the observed rate constants shown in Tables I and II are approximately 10%.

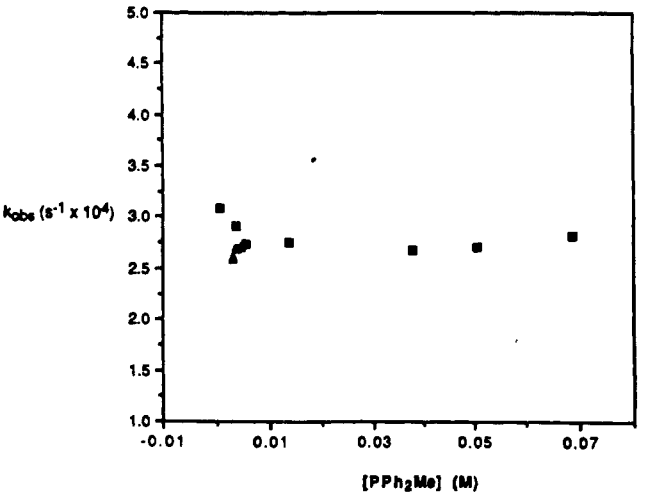


Figure 1. (■) Rate data for reaction of **5a** with PPh_2Me in toluene at 10 °C. (▼) Rate constants measured with added PPh_3.

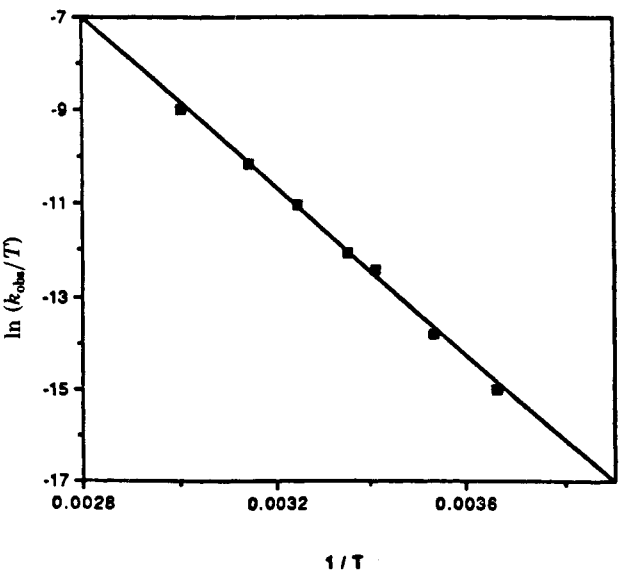
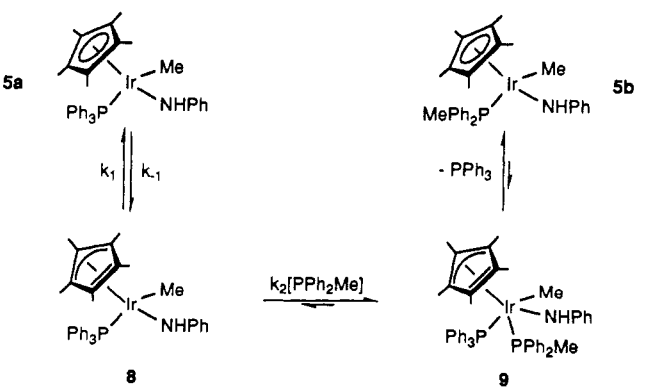


Figure 2. Eyring plot for reaction of **5a** with PPh_2Me in toluene.

Scheme II



The observed lack of inhibition by phosphine argues against loss of triphenylphosphine as the rate-determining step. However, this result could be explained if PPh_2Me is a much better trap for the intermediate than is PPh_3. To address this possible ambiguity, we determined the activation parameters for the reaction over the temperature range 0–60 °C. The data are shown in Table II. From the Eyring plot (Figure 2) $\Delta H^\ddagger = 18$ kcal/mol and $\Delta S^\ddagger = -10$ eu ($R^2 = 1.0$). The negative entropy of activation suggests

Table VI. $^{13}C\{^1H\}$ NMR Data for Cp*Ir(PPh_2Me)(Me)(X) Compounds[a]

compd	δ	mult	J, Hz	assgnt	compd	δ	mult	J, Hz	assgnt
1b (X = Me)	136.3	d	48.7	ipso	**5b** (X = NHPh)[b]	159.1			ipso N-C_6H_5
	132.8	d	10.3	o or m		137.4	d	49.1	ipso PPh_2Me
	129.1			p		134.0	d	10.3	o or m PPh_2Me
	127.8			*Ph*[d]		133.3	d	54.2	ipso PPh_2Me
	91.7	d	3.9	C_5Me_5		132.2	d	9.8	o or m PPh_2Me
	10.8	d	36.4	PPh_2*Me*		130.0			*Ph*
	8.2			C_5*Me_5*		129.4			*Ph*
	−21.9	d	8.9	Ir*Me*		128.5			*Ph*
2b (X = Cl)	134.4	d	50.9	ipso		128.0	d	9.9	o or m PPh_2Me
	134.1	d	52.6	ipso		127.7	d	9.6	o or m PPh_2Me
	133.5	d	9.9	o or m		116.5			N-*Ph*
	132.9	d	9.9	o or m		109.0			N-*Ph*
	130.1			p		92.4	d	3.5	C_5Me_5
	130.0			p		12.2	d	35.0	P-*Me*
	128.2	d	9.9	o or m		8.7			C_5*Me_5*
	128.0	d	10.0	o or m		−13.2	d	9.1	Ir-*Me*
	92.2	d	3.3	C_5Me_5	**6b** (X = OPh)[b]	168.3	d	2.3	ipso O*Ph*
	13.1	d	38.8	PPh_2*Me*		136.6	d	48.1	ipso P*Ph*
	8.3			C_5*Me_5*		134.4	d	10.6	o or m P*Ph*
	−17.0	d	10.3	Ir*Me*		132.0	d	9.3	o or m P*Ph*
3b (X = OAc)	177.9			*CO*		131.5	d	53.7	ipso P*Ph*
	136.7	d	50.2	ipso		130.6	d	2.0	pP*Ph*
	134.0	d	10.3	o or m		129.5	d	2.0	pP*Ph*
	133.2	d	10.3	o or m		128.7			pO*Ph*
	132.6	d	54.2	ipso		128.3	d	9.9	o or m P*Ph*
	129.9			p		128.0	d	9.7	o or m P*Ph*
	129.5			p		120.9			O*Ph*
	128.5			*Ph*[d]		113.0			O*Ph*
	127.8			*Ph*[d]		90.7	d	3.5	C_5Me_5
	90.6	d	3.1	C_5Me_5		11.1	d	36.1	P*Me*
	24.2			OC(O)*Me*		8.9			C_5*Me_5*
	12.8	d	34.7	P*Me*		−12.8	d	10.7	Ir-*Me*
	8.8			C_5*Me_5*					
	−10.6	d	9.9	Ir*Me*					
4b (X = CH_2Ph)[b]	153.4	d	2.4	ipso $CH_2C_6H_5$					
	138.1	d	49.3	ipso PPh_2Me					
	134.3	d	10.3	o or m PPh_2Me					
	133.3	d	48.6	ipso PPh_2Me					
	131.8	d	9.3	o or m PPh_2Me					
	129.9			*Ph*					
	129.0			*Ph*					
	128.7			*Ph*					
	128.0	d	8.5	o or m PPh_2Me[e]					
	127.8	d	8.5	o or m PPh_2Me[e]					
	127.1			CH_2*Ph*					
	121.9			CH_2*Ph*					
	92.6	d	3.0	C_5Me_5					
	11.1	d	36.3	P*Me*					
	8.2			C_5*Me_5*					
	−0.8	d	7.9	Ir*CH_2*Ph					
	−19.4	d	9.5	Ir*Me*					

[a] All spectra in C_6D_6 at 20 °C unless indicated. [b] CD_2Cl_2. [c] THF-d_8. [d] Partially obscured by C_6D_6. [e] Overlapping peaks.

that a dissociative mechanism is not occurring and is consistent with the lack of inhibition by PPh_3.

An alternative mechanism consistent with the observed data and with the behavior of the closely related hydride complexes is shown in Scheme II. Reversible slip of the η^5-C_5Me_5 ring to an η^3 (allyl-type) conformation would give the unsaturated intermediate (η^3-C_5Me_5)IrPPh_3(Me)(NHPh) (**8**). Coordination of PPh_2Me followed by loss of PPh_3 and return of the ring to the ordinary η^5 bonding mode yields the observed products. The reversible ring-slip may be assisted intramolecularly by the electron-donating amide ligand, which could stabilize the formally 16-electron metal center. Loss of free rotation of the C_5Me_5 ligand could account for the observed negative entropy of activation.

This mechanism is similar to that proposed for the phosphine-induced reductive elimination of aniline in the closely related hydride compound Cp*IrPPh_3(H)(NHPh). In each case, the first step is ring-slip, followed by coordination of phosphine to the new vacant coordination site, leading in this case to proposed intermediate **9**. The final step differs but in each case involves return of the Cp* to its normal η^5 configuration. In the hydride complex, elimination of aniline is observed, while in the methyl compound **9** the triphenylphosphine ligand is displaced. This mechanism suggests that, in the Cp*Ir system at least, N–H elimination is energetically more favorable than N–C elimination.

The reasons for this behavior are not yet completely clear, but analogous observations have been made in situations where comparable C–H and C–C reductive eliminations can occur. For example, in the closely related systems Cp*(PMe_3)Ir$(Me)_2$ and CP*(PMe_3)Ir(Me)(H), elimination of methane from the methyl hydride occurs at 130 °C, whereas the analogous elimination of ethane from the dimethyl complex is never observed before slow decomposition to intractable materials sets in at higher temperatures. This is an example of the general pattern that, other things being equal, C–C reductive elimination occurs less rapidly than C–H reductive elimination.[5] Our

results indicate that the relative roles played by hydrogen and carbon in reductive elimination reactions extend to bond-forming processes that involve heteroatoms. That is, reductive elimination of X–H from M(H)(X) complexes is apparently more rapid than reductive elimination of X–R from M(R)(X) complexes, whether X is a second carbon-bound fragment or a heteroatom.

η^5–η^3 interconversion of the cyclopentadienyl ligand and its relatives has often been observed or proposed on kinetic evidence.[6] In compounds similar to those described here, for example, Rerek and Basolo[7] showed that exchange of trialkylphosphine for CO in Cp′Rh(CO)$_2$ (Cp′ = Cp*, Cp) proceeded by an associative pathway and postulated the intermediate η^3-Cp′Rh(CO)(PR$_3$). The ring-slip proposed for the iridium amide compound described here differs from the previous examples, since it is not induced by an incoming ligand in an associative process.

Generality of Ligand Substitution. The phosphine exchange also occurs with the other iridium methyl compounds Cp*IrPPh$_3$(Me)(X), where X = Me, Cl, OPh, CH$_2$Ph, and OAc. The PPh$_2$Me-containing products, synthesized analogously from Cp*Ir(PPh$_2$Me)Cl$_2$, are spectroscopically very similar to the parent PPh$_3$ complexes. Where the Ir center is chiral, the nuclei in the two phenyl groups of the PPh$_2$Me ligand are nonequivalent and give rise to eight signals in the carbon NMR spectrum; this effect is not observed for Cp*Ir(PPh$_2$Me)Me$_2$.

The conditions required for exchange in C_6D_6 solution vary significantly with X. For X = NHPh, as described above, the reaction proceeds rapidly at room temperature. For X = OPh, the exchange is complete after 1 day at 45 °C. One day of heating at 85 °C is required when X = CH$_2$Ph, Cl, or OAc. The exchange proceeds slowly at 100 °C (~10% conversion after 1 day) when X = Me, and not at all when X = H; in this case heating at 100 °C slowly causes formation of the orthometalated compound Cp*Ir(PPh$_2$C$_6$H$_4$)(H)[8] with loss of methane. As observed for the anilide **5b**, acetate and phenoxide compounds **4b** and **6b** react further with PPh$_2$Me under the conditions required for phosphine exchange.

A similar rate ordering in a ligand substitution reaction was recently reported by Bryndza, Bercaw and co-workers in the Cp*Ru(PMe$_3$)$_2$X system.[9] Thermal exchange in these compounds proceeds by a dissociative pathway with loss of trimethylphosphine. In a comparison of ligands of the same size they observed the rate order NHPh > OPh > CH$_2$Ph. To rationalize this result, stabilization of the unsaturated 16-electron intermediate Cp*Ru(PMe$_3$)(X) by electronic donation from ligand X was invoked; the rates reflect the electron-releasing abilities of X.

The same argument can be used to rationalize the observed rate order in the Cp*IrPPh$_3$(Me)(X) system. The unsaturated intermediate (η^3-Cp*)IrPPh$_3$(Me)(X) should also be stabilized by electron-donating X groups, and the rate order we observe corresponds to that observed in the Ru system.

As in these proposed intermediates, amide lone pair to metal donation has previously been observed to stabilize formally coordinatively unsaturated species. For example, although the 16-electron Cp*Rh(*o*-C$_6$H$_4$O$_2$) forms 18-electron adducts with phosphines, the amide derivative Cp*Rh(*o*-C$_6$H$_4$(NH)$_2$) does not.[10] Similarly, PPh$_3$ dissociation from CpRe(PPh$_3$)(NO)(NHCH(Me)Ph) leading to the intermediate CpRe(NO)(NHR) was proposed to occur with anchimeric assistance of the amide lone pair.[11]

We have no direct evidence, however, that ligand exchange in Cp*IrPPh$_3$(Me)(X) occurs in general as it does for the anilide complex. In particular, for X = CH$_2$Ph and Me, which lack lone pairs, the substitution may occur by phosphine dissociation, as observed in the ruthenium series.[12] Steric effects are important in both series, as shown by the considerable rate difference between the benzyl and methyl compounds. The anomalous effect of the hydride ligand is also of interest. Although it should not differ too much electronically from a methyl group, phosphine exchange could not be observed in either Cp*IrPPh$_3$(Me)(H) or Cp*Ru(PMe$_3$)$_2$(H). We assume this is a steric effect.

Summary. Ligand substitution in the compounds Cp*IrPPh$_3$(Me)(X) occurs under mild conditions. Kinetic studies indicate that this exchange proceeds via an unsaturated intermediate formed by slip of the Cp* ring to an η^3 conformation, as proposed for the corresponding hydrides Cp*IrPPh$_3$(H)(X). The dependence of the ligand substitution rate on the nature of X can be rationalized by assuming that electron-donating X groups will stabilize the ring-slipped intermediate. As amide and alkoxide ligands are better donors than alkyl groups, the greater reactivity of these complexes as compared to the related alkyl and hydride compounds can be explained at least in part by the accessibility of the coordinatively unsaturated ring-slipped intermediate.

Experimental Section

General Considerations. Unless otherwise noted, all reactions and manipulations were performed in dry glassware under nitrogen atmosphere in a Vacuum Atmospheres 553-2 drybox equipped with an M6-40-1H Dri-train or by using standard Schlenk techniques.

All ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on 300-, 400- or 500-MHz instruments at the University of California, Berkeley NMR facility. The 300-MHz instrument was constructed by Rudi Nunlist and interfaced with a Nicolet 1280 computer. The 400- and 500-MHz machines were commercial Bruker AM series spectrometers. ^{1}H and ^{13}C NMR chemical shifts are reported in parts per million downfield from tetramethylsilane. ^{31}P NMR chemical shifts are given in parts per million downfield from 85% H$_3$PO$_4$. Coupling constants are given in hertz. Infrared spectra were recorded on a Perkin-Elmer Model 1550 Fourier transform spectrometer. Infrared bands are reported in inverse centimeters. Melting points are uncorrected and were determined with a Thomas-Hoover Unimelt capillary melting-point apparatus. Elemental analyses were conducted by the UC Berkeley Microanalysis Facility, and mass spectra were recorded by the UC Berkeley Mass Spectrometry laboratory on AEI MS-12 and Kratos MS-50 spectrometers. Mass spectral peaks are reported for the most abundant Ir isotopes ^{193}Ir and ^{191}Ir.

Toluene, benzene, and THF were distilled from sodium/benzophenone. Pentane was distilled from lithium aluminum hydride. Ethanol was distilled from Mg(OEt)$_2$. Hexamethyldisiloxane was distilled from calcium hydride. Diphenylmethylphosphine was distilled from sodium. Anilinium hydrochloride was recrystallized from ethanol/ether. Lithium anilide was prepared in toluene from butyllithium and aniline, which was distilled from calcium hydride. Potassium and sodium phenoxide

(5) Theorists have suggested that the more facile participation of hydrogen ligands in reductive elimination reactions may be due to the absence of a need for directionality in the hydrogen orbital involved in the elimination transition state: Low, J. J.; Goddard, W. A, III. *J. Am. Chem. Soc.* **1984**, *106*, 6928, 8321.

(6) For a review see: O'Connor, J. M.; Casey, C. P. *Chem. Rev.* **1987**, *87*, 307.

(7) Rerek, M. E.; Basolo, F. *J. Am. Chem. Soc.* **1984**, *106*, 5908.

(8) Janowicz, A. H. Ph.D. Thesis, University of California, Berkeley, 1982.

(9) Bryndza, H. E.; Domaille, P. J.; Paciello, R. A.; Bercaw, J. E. *Organometallics* **1989**, *8*, 379.

(10) Espinet, P.; Bailey, P. M.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1979**, 1542.

(11) Dewey, M. A.; Gladysz, J. A. *Organometallics* **1990**, *9*, 1351.

(12) As a reviewer has noted, we cannot rule out the possibility that π-benzyl coordination is involved in the substitution of the benzyl complex.

were made in toluene from phenol (vacuum distilled) and potassium hexamethyldisilazide and sodium metal, respectively. $[Cp^*IrCl_2]_2$ and $Cp^*PPh_3IrCl_2$ were prepared by literature methods.[13] Unless otherwise noted, all other reagents were used as received from commercial suppliers. Unless indicated, all reactions were carried out at ambient temperature.

Kinetics. All kinetics experiments were monitored by ultraviolet–visible spectroscopy using a Hewlett-Packard 8450A instrument equipped with a 89100A temperature controller. Standard solutions were prepared in the drybox in volumetric flasks and stored in the drybox freezer at −40 °C. Individual runs were prepared in the drybox by transferring aliquots of cold standard solutions using volumetric pipets into a quartz cuvette which was sealed with a Kontes high-vacuum stopcock, removed from the box, and placed in the spectrometer. It was allowed to reach temperature equilibrium with the cell holder before data were acquired. The solution in the cuvette was stirred with a micro stir bar, and a stream of nitrogen was passed through the cell holder to prevent condensation of water on the cell surface.

The reaction of $Cp^*IrPPh_3(Me)(NHPh)$ with PPh_2Me was monitored both at 380 nm (growth of product) and at 470 nm (disappearance of starting material), and consistent results were obtained. Reactions were observed for at least 3 half-lives.

Plots of absorbance vs time were fit by using the NEGINF and INFIN programs by Eric Wasserman of these laboratories to the increasing exponential function $y = A_1(1 - \exp(-A_2x)) + A_3$, where y = absorbance and x = time, or the decreasing exponential $y = A_1(\exp(A_2x)) + A_3$. From the least-squares fits, the observed rate is A_2.

$Cp^*IrPPh_3(Me)_2$ (1a). MeLi (1 mL of a 1.6 M solution in Et_2O, 1.6 mmol) was added with stirring to an orange slurry of $Cp^*IrPPh_3Cl_2$ (500 mg, 0.758 mmol) in 100 mL of THF. A homogeneous yellow-orange solution formed immediately. After 1 h of stirring, the solution was filtered through a bed of Alumina III on a frit and the remaining solids were washed with THF. Removal of the solvent from the filtrate in vacuo afforded yellow microcrystals of **1a** (323 mg, 69%): $^{31}P\{^1H\}$ NMR (C_6D_6) δ 10.6; IR (KBr) 3050, 2900, 1432, 1093, 705, 696, 544 cm^{-1}. Anal. Calcd for $C_{30}H_{36}IrP$: C, 58.13; H, 5.87. Found: C, 58.21; H, 5.68.

$Cp^*IrPPh_3(Me)(Cl)$ (2a). Acetone (50 mL; no drying or other purification is necessary) was condensed into a flask containing **1a** (323 mg, 0.522 mmol), anilinium chloride (68 mg, 0.52 mmol), and a stir bar. Upon thawing, the pale yellow slurry was stirred at room temperature; gas evolution was observed. After 40 min, the volatile materials were removed in vacuo to yield a yellow-orange solid. Recrystallization from toluene/pentane at −40 °C afforded 240 mg (72%) of yellow crystals of **2a**: $^{31}P\{^1H\}$ NMR (C_6D_6) δ 5.1; IR (C_6D_6) 3060, 3020, 2880, 1480, 1440 (s), 1090, 1030, 750 (s), 700 (vs) cm^{-1}. Anal. Calcd for $C_{29}H_{33}ClIrP$: C, 54.41; H, 5.20. Found: C, 54.49; H, 5.31.

$Cp^*IrPPh_3(Me)(OAc)$ (3a). The iridium methyl chloride complex **2a** (107 mg, 0.167 mmol) and silver acetate (354 mg, 2.12 mmol) were stirred in 20 mL of toluene in the dark for 5 days. The resulting slurry was filtered though Celite; the yellow filtrate was evaporated in vacuo. Recrystallization from toluene/hexane at −40 °C afforded 74 mg (67%) of yellow crystals: mp 205–210 °C dec; $^{31}P\{^1H\}$ NMR (C_6D_6) δ 15.6; IR (KBr) 3053, 2950, 2893, 1625 (vs), 1594, 1483, 1435, 1363, 1310, 1094, 702, 537 cm^{-1}. Anal. Calcd for $C_{31}H_{36}IrO_2P$: C, 56.08; H, 5.48. Found: C, 56.18; H, 5.72. FAB-MS (18-crown-6): m/e 664/662, $(M)^+$; 605/603, $(M - OAc)^+$.

$Cp^*IrPPh_3(Me)(CH_2Ph)$ (4a). The iridium methyl chloride complex **2a** (98 mg, 0.15 mmol) was slurried in 20 mL of ether, and benzyl magnesium chloride (0.2 mL of a 1 M solution in ether; 0.2 mmol) was added dropwise with vigorous stirring. After 10 min the yellow slurry became homogeneous and turned orange. After 80 min the orange solution was filtered through Alumina III on a frit. The light orange powder obtained by removing the solvent from the filtrate in vacuo was recrystallized from a concentrated toluene solution at ambient temperature to give 42 mg of yellow crystals of **4a**. A second crop (10 mg, total yield 49%) was obtained from toluene at −40 °C. An analytical sample, crystallized from toluene at −40 °C, was shown by ^1H NMR spectroscopy to contain 0.25 equiv of toluene. Mp: 172–177 °C dec. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 8.4. IR (KBr): 3055, 2908, 2812, 1487, 1433, 1092, 749, 698, 540, 515 cm^{-1}. Anal. Calcd for $C_{36}H_{40}IrP \cdot 0.25$(toluene): C, 63.06; H, 5.90. Found: C, 63.03; H, 5.80. FAB-MS (sulfolane): m/e 697/695, 696/694, 695/693 (overlapping signals due to $(MH)^+$, $(M)^+$, and $(M - H)^+$); 681/679, $(M - Me)^+$; 605/603, $(M - CH_2Ph)^+$.

$Cp^*IrPPh_3(Me)(NHPh)$ (5a). $Cp^*IrPPh_3(Me)(Cl)$ (**2**) (1047 mg, 1.64 mmol) and LiNHPh (500 mg, 5.06 mmol) were dissolved in 40 mL of THF and sealed in a glass bomb. The orange solution was heated to 85 °C for 3.5 h. The THF was removed in vacuo from the resulting dark orange-brown solution. The orange-brown residue was extracted with toluene and filtered through a frit. The dark orange filtrate was concentrated, layered with pentane and cooled to −40 °C to afford 909 mg (80%) of **5a** as an orange powder: $^{31}P\{^1H\}$ NMR (THF-d_8) δ 8.9; IR (KBr) 3351, 3057, 2919, 1486, 1093, 695 cm^{-1}. Anal. Calcd for $C_{35}H_{36}IrNP$: C, 60.32; H, 5.65; N, 2.01. Found: C, 60.01; H, 5.73; N, 1.94. FAB-MS (sulfolane): m/e 697/695, $(M)^+$; 605/603, $(M - NHPh)^+$.

$Cp^*IrPPh_3(Me)(OPh)$ (6a). The iridium methyl chloride complex **2a** (108 mg, 0.169 mmol) and sodium phenoxide (154 mg, 1.33 mmol) were dissolved in THF (10 mL) in a glass bomb, which was sealed and heated in a 65 °C oil bath. The progress of the reaction was monitored by $^{31}P\{^1H\}$ NMR spectroscopy of aliquots of the reaction mixture. After 16 days the solvent was removed in vacuo and the yellow solid extracted with toluene and recrystallized from this solvent at −40 °C to give 76 mg of yellow microcrystals (64%). Alternatively, acetate complex **3a** (115 mg, 0.171 mmol) and PhOK (40 mg, 0.30 mmol) were dissolved in 20 mL of THF. The yellow solution was placed in a bomb, which was heated in an 85 °C oil bath for 1 day. The solvent was removed in vacuo and the yellow residue extracted with toluene and filtered through a frit to remove the white solid. Concentration and cooling (to −40 °C) of the toluene solution gave 85 mg (71%) of **6a** as yellow crystals. Recrystallization from toluene at −40 °C gave yellow crystals, which were shown by ^1H NMR spectroscopy to contain toluene. Dissolution of this material in benzene followed by lyophilization removed the toluene but yielded a yellow solid that contained 0.5 equiv of benzene, as shown by ^1H NMR integration. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 7.1. IR (KBr): 3054, 2920, 1584, 1482, 1435, 1285, 697, 536 cm^{-1}. Anal. Calcd for $C_{35}H_{38}IrOP \cdot 0.5$(benzene): C, 61.92; H, 5.62. Found: C, 62.03; H, 5.47.

$Cp^*IrPPh_3(Me)(H)$ (7). Freshly distilled ethanol (15 mL) was condensed at −196 °C into a flask containing complex **2a** (68 mg, 0.11 mmol) and sodium ethoxide (10 mg, 0.15 mmol). Upon thawing, the yellow slurry was stirred at room temperature for 90 min, resulting in a clear, homogeneous yellow solution. On further stirring, the color bleached to a lighter yellow. After 6 days the solvent was removed in vacuo to give a yellow solid. This was extracted with pentane and filtered through a frit to afford a yellow solution, which was concentrated and cooled to −40 °C to yield 53 mg (82%) of yellow crystals of **7** in two crops: $^{31}P\{^1H\}$ NMR (C_6D_6) δ 20.1; IR (KBr) 3053, 2973, 2950, 2907, 2097, 1480, 1434, 1094, 697 cm^{-1}. Anal. Calcd for $C_{29}H_{34}IrP$: C, 57.49; H, 5.67. Found: C, 57.22; H, 5.82.

$Cp^*Ir(PPh_2Me)Cl_2$.[14] In the air, a glass bomb was loaded with $[Cp^*IrCl_2]_2$ (1010 mg, 1.27 mmol) and 100 mL of methylene chloride. The bomb was sealed and the orange solution subjected to two freeze–pump–thaw cycles on the vacuum line. In the drybox, 510 mg of diphenylmethylphosphine (2.54 mmol) was added as a solution in 1 mL of hexane. The bomb was resealed and heated at 45 °C for 1.5 h. The resulting orange solution was worked up in the air by filtration through Celite to remove insoluble yellow material. The clear orange filtrate was evaporated under reduced pressure and the resulting orange powder extracted with 80 mL of hexane in four portions, to remove excess phosphine. The residual hexane was filtered off and the orange solid recrystallized from methylene chloride/hexane at −20 °C to give an orange powder. This was collected on a frit and washed with hexane to yield 1203 mg of orange powder (79%): mp >235 °C;

(13) For $[Cp^*IrCl_2]_2$ see: Ball, R. G.; Graham, W. A. G.; Heinekey, D. M.; Hoyano, J. K.; McMaster, A. D.; Mattson, B. M.; Michel, S. T. *Inorg. Chem.* **1990**, *29*, 2023. For $Cp^*IrPPh_3Cl_2$ see: Kang, J. W.; Moseley, K.; Maitlis, P. M. *J. Am. Chem. Soc.* **1969**, *91*, 5970.

(14) Independently prepared and characterized in these laboratories. Newman, L. J.; Bergman, R. G. Unpublished results.

$^{31}P\{^1H\}$ NMR ($CDCl_3$) δ −5.5; IR (C_6H_6) 3080, 3030, 2940, 2860, 1475, 1100, 900 cm^{-1}. Anal. Calcd for $C_{23}H_{28}IrCl_2P$: C, 46.15; H, 4.72. Found: C, 46.16; H, 4.79.

Cp*Ir(PPh_2Me)Me_2 (1b). The orange dichloride complex Cp*Ir(PPh_2Me)Cl_2 (1100 mg; 1.84 mmol) was slurried in 60 mL of THF, and MeLi (2.8 mL of a 1.4 M solution in ether; 3.9 mmol) was added dropwise. The solution became homogeneous and turned yellow-orange. The mixture was stirred for 1 h and then filtered through Alumina III on a frit; the support was washed with 20 mL of THF. The THF was evaporated from the clear yellow filtrate to give 924 mg of yellow powder (90%): mp 115–120 °C; $^{31}P\{^1H\}$ NMR (C_6D_6) δ −6.7; IR (KBr) 3073, 3056, 2943, 2912, 2872, 1432, 1093, 888, 879, 744, 714, 696, 315, 490, 448 cm^{-1}. Anal. Calcd for $C_{25}H_{34}IrP$: C, 53.83; H, 6.16. Found: C, 54.06; H, 6.24. FAB-MS (sulfolane): *m/e* 558/556, $(M)^+$.

Cp*Ir(PPh_2Me)(Me)(Cl) (2b). As in the synthesis of PPh_3 analogue **2a**, dimethyl complex **1b** (924 mg, 1.66 mmol) and anilinium chloride (215 mg, 1.66 mmol) were stirred in 60 mL of acetone for 1.5 h. The acetone was removed in vacuo, and the yellow-orange solid was placed under high vacuum for 1 day to remove excess aniline. This left 796 mg of yellow powder (83%): $^{31}P\{^1H\}$ NMR (C_6D_6) δ −6.5; IR (KBr) 3055, 2974, 2949, 2915, 1436, 1099, 892, 750, 725, 697, 513 cm^{-1}. Anal. Calcd for $C_{24}H_{31}IrPCl$: C, 49.85; H, 5.42. Found: C, 50.21; H, 5.51. FAB-MS (nitrophenyl octyl ether): *m/e* 578/576, $(M)^+$; 563/561, $(M - Me)^+$.

Cp*Ir(PPh_2Me)(Me)(OAc) (3b). Methyl chloride complex **2b** (100 mg, 0.173 mmol) and silver acetate (327 mg, 1.96 mmol) were stirred in 20 mL of toluene in the dark for 2 days. The slurry was filtered through Celite; the yellow filtrate was concentrated and cooled to give 53 mg of yellow crystals (51%). An analytical sample was obtained from toluene at −40 °C. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 1.1. IR (KBr): 2949, 2919, 2892, 1615 (s), 1435, 1361, 1314, 889, 696 cm^{-1}. Anal. Calcd for $C_{26}H_{34}O_2IrP$: C, 51.89; H, 5.71. Found: C, 51.97; H, 5.59.

Cp*Ir(PPh_2Me)(Me)(CH_2Ph) (4b). The methyl chloride complex **1b** (66 mg, 0.11 mmol) was dissolved with stirring in 20 mL of Et_2O. Benzyl magnesium chloride (0.12 mL of a 1 M Et_2O solution, 0.12 mmol) was added dropwise to the yellow solution, which was stirred for 1.5 h and the filtered through Alumina III on a frit; the support was washed with ether. The combined yellow filtrate was evaporated in vacuo and the resulting yellow oil recrystallized from $(TMS)_2O$ at −40 °C to afford a yellow solid (44 mg, 61%), which became an oil at ambient temperature and could not be induced to crystallize. Yellow crystals for analysis were obtained by slow (weeks) crystallization from toluene at −40 °C. $^{31}P\{^1H\}$ NMR (C_6D_6): δ −7.8. IR (KBr): 3051, 2909, 1595, 1486, 1434, 1094, 885, 698, 512 cm^{-1}. Anal. Calcd for $C_{31}H_{38}IrP$: C, 58.74; H, 6.05. Found: C, 58.91; H, 6.01.

Cp*Ir(PPh_2Me)(Me)(NHPh) (5b). The methyl chloride **2b** (90 mg, 0.16 mmol) and LiNHPh (25 mg, 0.25 mmol) were dissolved in 15 mL of THF, and the yellow solution was sealed in a glass bomb, which was heated to 85 °C for 16 h. The solvent was removed in vacuo, and the orange-brown residue was extracted with pentane, filtered, concentrated, and cooled to −40 °C to give 46 mg of orange microcrystals (56%). A yellow powder suitable for analysis was obtained by a second recrystallization from pentane at −40 °C. $^{31}P\{^1H\}$ NMR (C_6D_6): δ −0.3. IR (KBr): 3352, 2919, 2881, 1596, 1487, 1434, 890, 695, 514 cm^{-1}. Anal. Calcd for $C_{30}H_{37}NIrP$: C, 56.75; H, 5.89; N, 2.21. Found: C, 56.24; H, 5.92; N, 2.24.

Cp*Ir(PPh_2Me)(Me)(OPh) (6b). Methyl acetate complex **4b** (176 mg, 0.29 mmol) and potassium phenoxide (105 mg, 0.80 mmol) were dissolved in THF (20 mL) and stirred. After 2 days phosphorus NMR spectroscopy of an aliquot indicated the reaction was not complete; an additional 20 mg of fresh KOPh was added. After 4 days the THF was removed in vacuo. The yellow oil was extracted with toluene, filtered through a frit, concentrated, layered with pentane, and cooled. After 1 day yellow oil formed. This was separated from the mother liquor, which on further cooling deposited 104 mg of yellow crystals (56%): $^{31}P\{^1H\}$ NMR (C_6D6) δ 0.4; IR (KBr) 3054, 2921, 1584, 1479, 1285, 1100, 891, 751, 697, 511 cm^{-1}. Anal. Calcd for $C_{30}H_{36}IrOP$: C, 56.67; H, 5.72. Found: C, 56.94; H, 6.00.

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