of the kinetically favored product, i.e., the trans isomer. Due to the length of the chelate backbone the trans isomer is not monomeric—dimeric 18-membered macrocycles being the preferred conformation.

Attempts to separate the trans species by column chromatography or vacuum sublimation failed.

Conclusions

The synthetic procedures outlined in this paper allow the synthesis of novel unsymmetrical bis(phosphines) with long flexible chelate backbones of the type $Ph_2P(CH_2)_nPR_2$ and $Ph_2P(CH_2)_nP(R)Ph$ (R = alkyl) and bis(chiral phosphines) of the type $Ph(R)P(CH_2)_nP(R)Ph$ (R = alkyl), ligands of great interest in homogeneous catalysis and asymmetric synthesis. The ligand synthesized and examined in this study, $Ph_2P(CH_2)_6P(Et)Ph$, can form cis or trans complexes with platinum(II) depending upon the reaction conditions employed and the starting materials used. The chemical shift difference between the two phosphorus nuclei (ca. 2 ppm) does not allow complete analysis of the ^{31}P NMR spectrum of the trans platinum(II) complex of the ligand. This and other observations[45] make it clear that the chemical shift separation between two chemically and magnetically nonequivalent phosphorus nuclei should be greater than 12 ppm to allow complete resolution at 35.4-MHz field strength for trans bis(phosphine) complexes.

Shaw has pointed out[4] that there are many examples where long-chain flexible bidentate ligands preferentially give open-chain polynucear rather than large-ring chelate complexes, and the formation of chelate rings vs. open-chain isomers can be explained in terms of ring strain and entropy factors. However, the formation of cis and trans isomers in these cases cannot be rationalized on these grounds alone. While it is certainly true that the presence of bulky terminal substituents on phosphorus may favor the formation of the trans-chelated complex over its cis analogue, many trans-chelated complexes have been synthesized with phosphorus,[2] arsenic,[29,30] and sulfur[31] donor atoms which do not possess bulky terminal substituents, indicating that other factors may play a vital role in determining the stereochemistry of transition-metal bis(phosphine) complexes.

Complexes of the type *cis*-$[Pt(PR_3)_2Cl_2]$ can be considered to be products of thermodynamic control—a stronger platinum–phosphorus bond being formed when the coordinated phosphorus is trans to a chlorine (which possesses a weak trans influence). A general preparation for this type of complex is the reaction of potassium tetrachloroplatinate (II) with the ligand in a polar solvent. In certain cases, for instance, when R = alkyl, a cis/trans mixture of isomers will either result at room temperature or result after heating the product of the reaction.[43,54] However, when one or two of the substituents is a phenyl group, the product is exclusively the cis isomer, indicating that the basicity of the donor phosphorus may play a role in determining the reaction product.

For ligands that possess two phenyl groups attached to the donor phosphorus atom, it is necessary to react the phosphine with a precursor that will give the product of kinetic control[44]—for example, Zeise's salt[55] or the chlorine-bridged dimer $[Pt_2(PR_3)_2Cl_4]$[43]—in order to obtain the trans isomer. The choice of such a precursor is not necessary for the synthesis of trans-palladium(II)–phosphine complexes; the product of kinetic control (the trans isomer) is formed in almost all cases.[2,56–61] These results and the results obtained in this paper indicate that the choice of a suitable complex precursor is critical for the synthesis of trans-chelated complexes of platinum(II), and such complexes can be readily synthesized by the employment of kinetically labile starting substrate.

Registry No. I, 82195-38-8; II, 83152-25-4; **3a**, 83152-26-5; **3b**, 83152-29-8; $[Br(CH_2)_6PPh_3]Br$, 83152-22-1; $[Ph_2(Et)P(CH_2)_6PPh_3]Br_2$, 83152-23-2; $EtPh(O)P(CH_2)_6P(O)Ph_2$, 83152-24-3; *cis*-$[Ph_2P(CH_2)_6P(Et)Ph]PtCl_2$, 83152-27-6; *cis*-$(PhCN)_2PtCl_2$, 15617-19-3; *trans*-$([Ph(Et)P(CH_2)_6P(Et)Ph]PtCl_2)_2$, 83152-28-7; 1,6-dibromohexane, 629-03-8; triphenylphosphine, 603-35-0; diphenylethylphosphine, 607-01-2; 1,6-bis(diphenylphosphino)hexane, 19845-69-3; ethyl iodide, 75-03-6; Zeise's salt, 16405-35-9; potassium tetrachloroplatinate(II), 10025-99-7.

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Contribution from the Departments of Chemistry, Sterling Chemistry Laboratory, Yale University, New Haven, Connecticut 06511, and Manhattanville College, Purchase, New York 10577

^{13}C NMR Spectra of Some New Iridium(I) Complexes: Evidence for Reductive Character in H_2 Addition and the Cis and Trans Influences of Nitriles

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Syntheses of the new complexes $[Ir(cod)(PPh_3)(RCN)]A$ and $[IrH_2(cod)(PPh_3)(RCN)]A$ (cod = 1,5-cyclooctadiene; A = BF_4; R = Me, *p*-$MeOC_6H_4$, C_6H_5, *p*-$CH_3COC_6H_4$, and *p*-$NO_2C_6H_4$) are reported. ^{13}C NMR spectroscopy suggests the addition of H_2 takes place with an increase, rather than the more usual decrease, of electron density at the metal. The data also reveal the presence of cis and trans influences of R on the cod δ(C(vinyl)), which are in the same direction, the trans being ca. 3.5 times greater than the cis influence.

The term oxidative addition as applied to eq 1 carries with

$$\underset{1}{L_nM} + XY \rightarrow \underset{2}{L_nM(X)(Y)} \qquad (1)$$

it the implication that the metal has been oxidized in the process. We have suggested that some additions of this type seem not to give rise to oxidation of the metal but rather to reduction.[3,4] In these cases the electron density at the metal

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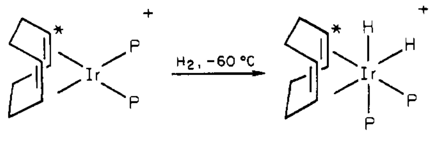
is higher in **2** than in **1**, rather than the more usual reverse situation. Vaska[5] was the first to consider this problem in relation to his well-known $[IrX(CO)(PPh_3)_2]$ (**3**, X = halide). He attempted to follow electron density changes at Ir by studying $\Delta\nu(CO)$ for reaction 1 by IR spectroscopy. In the vast majority of cases, a positive $\Delta\nu(CO)$ was observed, and the addition was therefore held to be oxidative, but in two cases, the additions of ethylene and acrylonitrile to **3** (X = I), a negative $\Delta\nu(CO)$ was observed. The interpretation of this shift as resulting from a reduction of the metal is complicated by the trans effect, because in Vaska's case the CO is trans to X in the starting complex but trans to the addendum in the adduct. Further anomalous results, not consistent with the classical idea of an oxidative addition, have appeared recently.[6]

The ^{13}C NMR spectra of metal olefin complexes have also been used to estimate the electron density at the metal,[7] and our recent observations[4] suggest that the addition of hydrogen to the complexes $[Ir(cod)(PPh_3)_2]^+$ (cod = 1,5-cyclooctadiene) and $[Ir(cod)(PMePh_2)_2]^+$ may be reductive in character. The formation of the cis dihydride is accompanied by a decrease in the ^{13}C chemical shift of the cyclooctadiene carbons ($\Delta\delta = -3.3$ and -3.7, respectively) that remain trans to the phosphine (marked with an asterisk in eq 2). These results



(2)

are in contrast with the observed oxidative character for addition of HX (X = Cl, Br, I; $\Delta\delta = 10.8, 10.1, 10.1$) to $[Ir(cod)(PMePh_2)_2]^+$. This use of ^{13}C NMR shifts to estimate electron density changes at the metal may only be valid within a range of similar complexes,[7] as the origin of vinyl ^{13}C NMR shifts in olefin complexes is controversial.[7b]

Since dihydrides of the type *cis*-$[Ir(cod)LL'H_2][PF_6]$ (L = phosphine, L′ = L or amine) have been shown to be intermediates in the catalytic hydrogenation of hindered olefins,[7] the nature of the hydrogen addition process and the reactivity of these intermediates are of considerable interest. However, the H_2 adducts of these cations are stable only at low temperature; when they are warmed, hydrogen is transferred to the coordinated cod:[3]

$$Ir(cod)(PPh_3)_2{}^+ \xrightarrow[-80\ °C]{H_2} [IrH_2(cod)(PPh_3)_2]^+ \xrightarrow[0\ °C]{H_2} [Ir_2H_5(PPh_3)_4]^+ + H^+ + coe + coa \quad (3)$$

coe = cyclooctene; coa = cyclooctane

Table I. ^1H NMR Data for the Complexes $[Ir(cod)(PPh_3)L'][BF_4]$ (213 K, CD_2Cl_2)

	δ	
complex	cod vinyl	CH_3
$[Ir(cod)(PPh_3)(CH_3CN)]^+$	5.0	2.0
	3.4	
$[Ir(cod)(PPh_3)(p\text{-}CH_3OC_6H_4CN)]^+$	5.2	3.8
	3.5	
$[Ir(cod)(PPh_3)(C_6H_5CN)]^+$	5.1	
	3.5	
$[Ir(cod)(PPh_3)(p\text{-}CH_3C(O)C_6H_4CN)]^+$	5.5	2.7
	3.5	
$[Ir(cod)(PPh_3)(p\text{-}NO_2C_6H_4CN)]^+$	5.5	
	3.7	
$[Ir(cod)(PPh_3)py]^+$	4.4	
	3.5	

Table II. ^1H NMR Data for the Complexes *cis*-$[Ir(cod)(PPh_3)L'H_2][BF_4]$ (213 K, CD_2Cl_2)

	δ[a]	
complex	cod vinyl	Ir-H
$[Ir(cod)(PPh_3)(CH_3CN)H_2]$	5.5	−13.4 d (21)
	4.9	−16.4 d (16)
	4.1[b]	
$[Ir(cod)(PPh_3)(p\text{-}CH_3OC_6H_4CN)H_2]^+$	5.6	−13.0 d (21)
	5.1	−15.9 d (11)
	4.4	
	4.2	
$[Ir(cod)(PPh_3)(C_6H_5CN)H_2]^+$	5.6	−13.1 d (17)
	5.1	−15.9 d (15)
	4.4	
	4.2	
$[Ir(cod)(PPh_3)(p\text{-}CH_3C(O)C_6H_4CN)H_2]^+$	5.5	−13.3 d (21)
	5.1	−15.9 d (12)
	4.6	
	4.4	
$[Ir(cod)(PPh_3)(p\text{-}NO_2C_6H_4CN)H_2]^+$	5.6	−13.2 d (19)
	5.1	−15.8 d (13)
	4.6	
	4.5	
$[Ir(cod)(PPh_3)pyH_2]^+$	*c*	−11.8 d (17)
		−17.3 d (13)

[a] Reported as position, multiplicity, and J_{PH} (Hz, in parentheses). [b] Integration: two carbons. [c] Obscured by the presence of unchanged 4.

Table III. ^{13}C NMR Data for $[Ir(cod)(PPh_3)L'][BF_4]$ (210 K, CD_2Cl_2)

	δ[a]	
complex	cod vinyl	cod allyl
$[Ir(cod)(PPh_3)(CH_3CN)]^+$	92.8 d (11)	32.0
	67.1	29.2
$[Ir(cod)(PPh_3)(p\text{-}CH_3OC_6H_4CN)]^+$	92.6 d (8)	31.9
	67.9	29.1
$[Ir(cod)(PPh_3)(C_6H_5CN)]^+$	93.2 d (11)	32.3
	69.3	29.5
$[Ir(cod)(PPh_3)(p\text{-}NO_2C_6H_4CN)]^+$	93.5 d (11)	32.2
	70.7	29.4

[a] Reported as position, multiplicity, and J_{PC} (Hz, in parentheses).

Here we report the synthesis and NMR spectra of the series of complexes $[Ir(cod)(Ph_3P)L][BF_4]$ (**4**, L = CH_3CN, C_6H_5, *p*-$NO_2C_6H_4CN$, *p*-$MeCOC_6H_4CN$, *p*-$CH_3OC_6H_4CN$) designed to monitor the redox character of the H_2 addition and the catalytic activity of the hydrogen adduct (**5**) as a function of electron density at the metal site. These dihydrides have the advantage of improved thermal stability and can be isolated at room temperature as white solids. Another useful feature of these complexes is that the electron-donating character of L′ can be altered in an isosteric series, ArCN (Ar = *p*-$CH_3OC_6H_4$, C_6H_5, *p*-$NO_2C_6H_4$, or *p*-$MeCOC_6H_4$).

Results and Discussion

The complexes $[IrCl(cod)(PPh_3)]$, readily obtained[8] from PPh_3 and $[IrCl(cod)]_2$, react with $AgBF_4$ in CH_2Cl_2 containing an excess of L′ (L′ = RCN) to give the orange solutions. After filtration to remove the precipitated AgCl, the new complexes **4** were isolated with Et_2O (see Experimental Section). Their

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Table IV. ^{13}C NMR Data for $[Ir(cod)(PPh_3)L'H_2]BF_4$ (CD_2Cl_2, 210 K)

complex	δ(cod vinyl)	Δδ	δ(cod allyl)	Δδ′
$[Ir(cod)(PPh_3)(CH_3CN)H_2]^+$	88.1[b]	−5.1	30.8	−3.75
	87.3[b]		25.7	
	94.5		32.7	
	93[a]		31.3	
$[Ir(cod)(PPh_3)(p\text{-}CH_3OC_6H_4CN)H_2]^+$	88.4 d (5)	−4.2	30.1	−4.25
	87.1 d (7)		25.2	
	94.2		33.1	
	92.6		31.6	
$[Ir(cod)(PPh_3)(C_6H_5CN)H_2]^+$	89.0 d (8)	−4.8	30.6	−4.15
	87.8 d (8)		25.7	
	94.8		33.4	
	93.4		31.9	
$[Ir(cod)(PPh_3)(p\text{-}NO_2C_6H_4CN)H_2]^+$	89.4 d (9)	−4.7	30.4	−4.2
	88.2 d (11)		25.6	
	95.7		33.3	
	94.0		31.9	

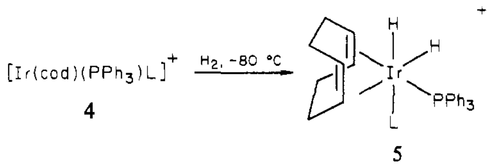
[a] Partially obscured. [b] Broad ($^2J_{PC}$ coupling).

identity follows from the microanalytical and ^{1}H (Table I) and ^{13}C NMR (Table III) data.

They are active hydrogenation catalysts, an aspect which is currently under study.

The ^{1}H NMR data for the complexes $[Ir(cod)(PPh_3)(RCN)]BF_4$ (**4**) listed in Table I show two cod vinyl ^{1}H NMR resonances, one at δ 4.4–5.5 for the cod vinyl group trans to the better π acceptor PR_3 and the other at δ 3.4–3.7 for the cod vinyl group trans to L′. This assignment of cod vinyl resonances is confirmed by the finding that, of the corresponding resonances in the ^{13}C NMR, the low-field one is a doublet, having a characteristic ^2J(P,C) trans coupling constant of 8–11 Hz. ^{1}H and ^{13}C resonances that can be assigned to the nitrile, the PPh_3, and the cod allyl resonances are also observed in each case.

The complexes **4** in CD_2Cl_2 at −80 °C all react with H_2 to give pale yellow or colorless solutions of the adducts **5** (eq 4).



(4)

Their identity follows from their NMR spectra. Two resonances assigned to Ir–H appear at δ −11.8 to 13.4 and −15.8 to −17.3, respectively. By analogy with related compounds,[9] the former can be assigned to Ir–H trans to cod and the latter to Ir–H trans to RCN. Each shows coupling to a cis-PPh_3 group; ^2J(P,H) = 11–21 Hz. Four vinyl C–H resonances are seen. We have previously shown that this occurs when the molecule lacks any plane of symmetry.[9] The ^{13}C NMR data confirm the assignment of the stereochemistry as **5** because four cod vinyl resonances are observed, the high-field ones showing ^2J(P,C) trans coupling of 5–11 Hz. In one case (L′ = MeCN), this splitting was not resolved.

The expected trans-influence order H > PPh_3 > RCN follows from the relative ordering of the cod vinyl resonances in the ^{13}C NMR spectra of **4** and **5**. More subtle effects can also be seen. The R substituent in the RCN ligand affects the position of the trans-cod vinyl resonance. The trans-influence order for R, $p\text{-}NO_2C_6H_4$ > C_6H_5 > $p\text{-}CH_3OC_6H_4$ > Me, shows a systematic variation, suggesting that the ^{13}C chemical shift may be a good measure of electron density changes at the metal in a closely related series of complexes such as this. More interestingly, the cod vinyl resonances cis to RCN also show parallel but smaller variations of chemical shift. In Figure 1, δ(C(cis)) is plotted against δ(C(trans)) for the cod vinyl groups cis and trans to L′. Although instrumental and solubility limitations prevented us from obtaining further data, it can be seen that the cis and trans influences are in the same direction and correlate well (correlation coefficient 0.91). The slope of the plot, 3.6, represents the ratio of the trans/cis influences. The origin and relative sign and magnitude of the cis and trans effects are still controversial[10] and probably depend on the way they are observed.

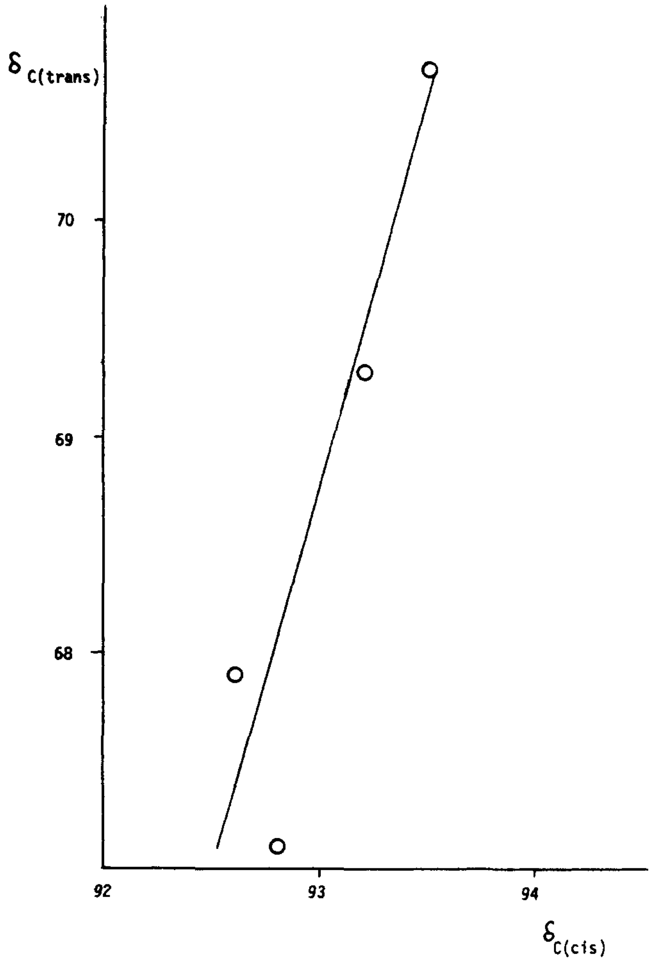


Figure 1. δ(C(cis)) against δ(C(trans)) for cod vinyl groups in **4** cis and trans to the nitrile ligand.

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[9] Crabtree, R. H.; Felkin, H.; Fillebeen-Khan, T.; Morris, G. E. *J. Organomet. Chem.* **1979**, *168*, 183.

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The same general effects can be seen in the six-coordinate adduct (**5**), but both cod vinyl groups are cis to L′, and no plot such as Figure 1 can be obtained. Nevertheless, inspection of the data (Table IV) suggests that the cod trans to H is more influenced by changes in L′ than is the cod trans to L.

A number of factors have probably contributed to our being able to see these unusual cis influences so clearly. We have used a relatively weakly bound ligand (cod), as such a ligand is probably rather more sensitive to electronic effects at the metal than a strongly bound ligand. cod ^{13}C NMR shifts are known to occur in an unusually wide range. We have used a closely related series of complexes, taking particular care to choose a sterically undemanding RCN group as the influencing ligand, a choice that reduces to a minimum any complicating steric perturbations.

When H_2 is added to give **5**, only one cod (C=C) group remains trans to PPh_3. It should be insensitive to a trans effect, and we have therefore calculated the change in resonance position of this group, listed as $\Delta\delta$ in Table IV. The values are negative by 4.2–5.1 ppm, suggesting that the coordination of H_2 causes an increase in the electron density at the metal. These H_2 additions, like those to $[Ir(cod)(PR_3)_2]A$, described previously,[4] appear to be reductive in character. Furthermore, the effect of electron density at the metal on the degree of reductive character is apparent within the series. The anisole nitrile, which is electron donating by resonance, shows the least reductive hydrogen addition.

The $\Delta\delta$ values for the complexes $[Ir(cod)(PR_3)_2]A$ (ca. −3.5 ppm) are somewhat less[4] than those for the complexes **4**. This is consistent with the stronger overall donor ability[11] of PR_3 relative to that of RCN, giving **4** the greater electrophilic character.

In associating $\Delta\delta$ values with metal electron density changes, we assume, as in our previous work,[4] that the other contributions to the shift do not affect $\Delta\delta$. Any excitation energy differences between **4** and **5** might affect the paramagnetic term contributing to the CH vinyl shift and lead to difficulties in interpretation. We have therefore examined the behavior of the cod allyl shift, where such differences should affect $\Delta\delta'$ ($\Delta\delta' = \Delta\delta$(cod allyl)) to a much lesser extent. We have not yet been able to assign the resonances by a definitive method but assume that they appear in the same order as do the corresponding cod vinyl resonances. The $\Delta\delta'$ values so obtained and shown in Table IV are, as expected, similar to, but generally smaller than, the $\Delta\delta$ values.

The strength of the M–cod bond may well be affected by the donor ability of the RCN ligand. We have preliminary evidence that this effect influences the temperature of transfer of coordinated H_2 to coordinated cod as well as the rate of catalytic hydrogenation of olefins with these catalyst precursors.[12]

Also shown in Tables I and II are data for the complexes **3** and **5** (Ar = p-$CH_3COC_6H_4$), for which only ^{1}H NMR data were obtained. The ^{1}H NMR data show qualitatively the same trends as noted above for the ^{13}C NMR data, except that the former show greater scatter.

Reactions with HX and X_2 are being investigated because our earlier work[4] showed that where such adducts can be obtained positive $\Delta\delta$ values are found, as expected. So far, only products lacking RCN have been isolated.

Conclusion

We have described a series of new cod complexes of iridium and have shown that both cis and trans influences can be observed by ^{13}C NMR for the cod vinyl resonances. These have the same sign, but the trans influence is ca 3.5 times larger than the cis influence. Hydrogen addition to the complexes gives relatively stable H_2 adducts in which the electron density at Ir seems to have increased rather than decreased on adduct formation, as judged by cod vinyl shifts. This is consistent both with our earlier work[4] and with work to be published[12] on equilibria involving H_2 and the complexes **4**.

Experimental Section

The starting materials were synthesized as previously described.[13] ^{13}C NMR spectra were recorded on a Bruker 67.6-MHz instrument (^{1}H NMR, 270 MHz). All operations were carried out in a nitrogen atmosphere with use of standard Schlenk tube techniques. Analyses were performed by Galbraith Laboratories, Knoxville, TN.

(Acetonitrile)(1,5-η-cyclooctadiene)(triphenylphosphine)iridium(I) Tetrafluoroborate. $Ir(cod)(PPh_3)Cl$ (300 mg) in dichloromethane (30 mL) and acetonitrile (2 mL) was treated with $AgBF_4$ (100 mg). The precipitated AgCl was filtered off and the filtrate reduced to about 10 mL. The orange product was precipitated with diethyl ether, washed with diethyl ether and pentane, and recrystallized from CH_2Cl_2/Et_2O (yield 86%). Anal. Calcd for $C_{28}H_{30}NPBF_4Ir$: C, 48.69; H, 4.37. Found: C, 48.44; H, 4.55.

(Benzonitrile)(1,5-η-cyclooctadiene)(triphenylphosphine)iridium(I) Tetrafluoroborate. This compound was prepared with use of the procedure described above, with substitution of 2 mL of benzonitrile for the acetonitrile. Anal. Calcd for $C_{33}H_{32}NPBF_4Ir\cdot{}^1/_2CH_2Cl_2$: C, 50.31; H, 4.12. Found: C, 50.37; H, 4.21.

The following orange crystalline complexes were prepared in similar yields by the same procedure using 0.5 mmol of the nitrile.

(p-Nitrobenzonitrile)(1,5-η-cyclooctadiene)(triphenylphosphine)iridium(I) Tetrafluoroborate. Anal. Calcd for $C_{33}H_{31}N_2O_2PBF_4Ir$: C, 49.69; H, 3.91. Found: C, 49.64; H, 4.17.

(p-Acetylbenzonitrile)(1,5-η-cyclooctadiene)(triphenylphosphine)iridium(I) Tetrafluoroborate. Anal. Calcd for $C_{35}H_{34}NOPBF_4Ir$: C, 52.90; H, 4.31. Found: C, 52.43; H, 4.39.

(p-Methoxybenzonitrile)(1,5-η-cyclooctadiene)(triphenylphosphine)iridium(I) Tetrafluoroborate. Anal. Calcd for $C_{34}H_{34}NOPBF_4Ir$: C, 52.17; H, 4.37. Found: C, 51.66; H, 4.49.

Preparation of the H_2 Adducts. $[Ir(cod)(PPh_3)L][BF_4]$ (L = CH_3CN, PhCN, p-$NO_2(C_6H_4)CN$, p-$CH_3C(O)C_6H_4CN$, p-$CH_3OC_6H_4CN$) (75 mg) were dissolved in degassed dichloromethane (5 mL, 0 °C). Hydrogen gas was bubbled through the solution for 5 min or until decolorization was complete. The crude white products were isolated with Et_2O and recrystallized from dichloromethane/ether under a hydrogen atmosphere. The dihydrides lose hydrogen in air or under vacuum to regenerate the original complex.

The complexes were too unstable for microanalysis or IR spectral studies, but with samples prepared in situ under H_2, ^{1}H and ^{13}C NMR spectra were obtained without H_2 loss if the samples were maintained at 213 K.

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Registry No. **4** (L = CH_3CN), 83115-16-6; **4** (L = C_6H_5CN), 83115-18-8; **4** (L = p-$NO_2C_6H_4CN$), 83115-20-2; **4** (L = p-$CH_3C(O)C_6H_4CN$), 83115-22-4; **4** (L = p-$CH_3OC_6H_4CN$), 83115-24-6; **5** (L = CH_3CN), 83134-40-1; **5** (L = p-$CH_3OC_6H_4CN$), 83115-26-8; **5** (L = C_6H_5CN), 83115-28-0; **5** (L = p-$CH_3C(O)C_6H_4CN$), 83115-30-4; **5** (L = p-$NO_2C_6H_4CN$), 83115-32-6; **4** (L = py), 83115-33-7; **5** (L = py), 83115-35-9; $Ir(cod)(PPh_3)Cl$, 12115-50-3; $AgBF_4$, 14104-20-2; acetonitrile, 75-05-8; benzonitrile, 100-47-0.

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