Unexpected Isomerization of a *cis*- into a *trans*-Dihydride Complex. A Neutral Late Transition Metal Complex as a Hydride Donor

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Reaction of $HIr(PPh_3)_3(CO)$ (**1**) with 1,3-bis[(diisopropylphosphino)methyl]benzene (**2**) in THF or benzene at 60 °C affords *trans*-$H_2Ir(CO)L$ (**3**; L = $C_6H_3(CH_2P(i\text{-}Pr_2)_2)$. The cationic complex $[HIr(PPh_3)(CO)L]Br$ (**5**) was obtained in the reaction of **1** with 1,3-bis[(diisopropylphosphino)methyl]-2-bromobenzene (**4**). Reaction of **5** with KO-*t*-Bu leads to the Ir(I) complex Ir(CO)L (**6**), which adds methyl iodide to form $IIr(CO)(CH_3)L$ (**7**). Addition of H_2 to **6** results in formation of *cis*-$(L)Ir(H)_2(CO)$ (**8**). This reaction is reversible, due to the rigid square-planar geometry of **6**. Under H_2 pressure **8** isomerizes into **3**, demonstrating *cis*- into *trans*-dihydride isomerization, which is unprecedented for octahedral complexes. The *trans*-dihydride six-coordinate complex **3** exhibits hydridic reactivity which is unusual for a neutral late transition metal complex and is due to the strong mutual *trans* influence of the hydride ligands. Various electrophiles ($[Ph_3C]BF_4$, PhC(O)Cl, CS_2, MeI) directly attack the hydride ligand of **3**, forming products of selective hydride transfer. Abstraction of the hydride ligand with the electrophiles affords the iridium complexes $[HIr(PPh_3)(CO)L]Br$ (**9**), HIr(Cl)(CO)L (**10**), HIr(CO)(SC(S)H)L (**11**), and HIr(I)(CO)L (**12**).

Introduction

The stability and reactivity modes of transition-metal hydrides, e.g. hydridic vs protonic reactivity, is of great general interest since a wide range of important catalytic and stoichiometric processes involve such compounds.[1] While *cis*-dihydride complexes are abundant, few stable *trans*-dihydride complexes have been reported.[2] This is thought to be a result of the large *trans* influence of the hydride ligand, rendering the *cis*-dihydride configuration more stable unless dominant steric factors disfavor it.

We report here a surprising isomerization of an octahedral iridium *cis*-dihydride complex into the corresponding *trans* complex (which was also synthesized independently), clearly attesting to the unexpected higher thermodynamic stability of the latter, although apparently no significant steric factors are involved. Also, while hydridic reactivity is known for early transition metals,[3] anionic complexes,[4] and some polyhydrides[4c] and clusters,[5] the iridium *trans*-dihydride reported here represents an unusual case of a neutral six-coordinate late transition metal complex possessing hydridic reactivity. This is exemplified in intermolecular hydride transfer reactions with various electrophiles.

Results

Synthesis and Characterization of *trans*-Ir(DIPPX)(H)$_2$(CO) (3). Careful choice of the metal precursors for cyclometalation of PCP ligands was shown to be critical when the phosphine substituents were less bulky than *t*-Bu.[6] The iridium hydride complex $HIr(PPh_3)_3(CO)$ (**1**) is known to reversibly dissociate a phosphine ligand in solution[7] to yield the four-coordinate sterically unsaturated *trans*-$HIr(PPh_3)_2(CO)$. Facile coordination of the PCP ligands to this intermediate is expected.

Reaction of equivalent amounts of $HIr(PPh_3)_3(CO)$ (**1**) and the ligand DIPPX (**2**; **D**i**I**so**P**ropyl**P**hosphino**X**ylene (1,3-bis[(diisopropylphosphino)methyl]benzene)) at 60 °C in THF or C_6H_6 gives **3** in nearly quantitative yield, as observed by $^{31}P\{^1H\}$ NMR (eq 1). A small amount of Ir(DIPPX)CO (**6**; 5−7%) was also formed (*vide infra*). We were not able to separate complex **3** from triphenylphosphine.[8]

Selected spectral data for complex **3** are given in Table 1. It gives rise to a singlet in $^{31}P\{^1H\}$ NMR centered

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(1) (a) Pearson, R. G. *Chem. Rev.* **1985**, *85*, 41. (b) Simões, J. A. M.; Beauchamp, J. L. *Chem. Rev.* **1990**, *90*, 629. (c) Angelici, R. J. *Acc. Chem. Res.* **1995**, *28*, 51. (d) Wang, D.; Angelici, R. J. *J. Am. Chem. Soc.* **1996**, *118*, 935.

(2) (a) Fryzuk, M. D.; MacNeil, P. *Organometallics* **1983**, *2*, 682. (b) Immirzi, A.; Musco, A.; Carturan, G.; Belluco, U. *Inorg. Chim. Acta* **1975**, *12*, L23. (c) Shaw, B. L.; Uttley, M. F. *J. Chem. Soc., Chem. Commun.* **1974**, 918. (d) Yoshida, T.; Otsuka, S. *J. Am. Chem. Soc.* **1977**, *99*, 2134. (e) Paonessa, R. S.; Trogler, W. C. *J. Am. Chem. Soc.* **1982**, *104*, 1138.

(3) For example see: (a) Sweet, J. R.; Graham, W. A. G. *Organometallics* **1982**, *1*, 982. (b) Sullivan, P. B.; Meyer, T. J. *Organometallics* **1986**, *5*, 1500. (c) Martin, B. D.; Warner, K. E.; Norton, J. R. *J. Am. Chem. Soc.* **1986**, *108*, 33.

(4) For a review see: (a) Darensbourg, M. Y.; Ash, C. E. *Adv. Organomet. Chem.* **1987**, *27*, 1. See also: (b) Kinney, R. J.; Jones, W. D.; Bergman, R. G. *J. Am. Chem. Soc.* **1978**, *100*, 7902. (c) Linn, D. E., Jr.; Halpern, J. *J. Am. Chem. Soc.* **1987**, *109*, 2969.

(5) $[(Ph_3P)CuH]_6$ reactivity: (a) Mahoney, W. S.; Brestensky, D. M.; Stryker, J. M. *J. Am. Chem. Soc.* **1988**, *110*, 291. (b) Mahoney, W. S.; Stryker, J. M. *J. Am. Chem. Soc.* **1989**, *111*, 8818.

(6) (a) Gorla, F.; Venanzi, L. M. *Organometallics* **1994**, *13*, 43 and references therein. (b) Gorla, F.; Togni, A.; Venanzi, L. M. *Organometallics* **1994**, *13*, 1607.

(7) (a) Harrod, J. F.; Gilson, D. F. R.; Charles, R. *Can. J. Chem.* **1969**, *47*, 2205. (b) Yagupsky, G.; Brown, C. K.; Wilkinson, J. *J. Chem. Soc. A* **1970**, 1392. (c) Harrod, J. F.; Hamer, G.; Yorke, W. *J. Am. Chem. Soc.* **1979**, *101*, 3987. (d) Harrod, J. F.; Yorke, W. *Inorg. Chem.* **1981**, *20*, 1156. (e) Malatesta, L.; Caglio, G.; Angoleta, M. *J. Chem. Soc.* **1965**, 6974. (f) Chatt, J.; Coffey, R. S.; Shaw, B. L. *J. Chem. Soc.* **1965**, 7391.

(8) All attempts to separate **3** from PPh_3 by crystallization failed. Chromatography on alumina or silica and using of $PdCl_2(CH_3CN)_2$ as a "phosphine sponge" also did not result in separation of **3** from PPh_3.

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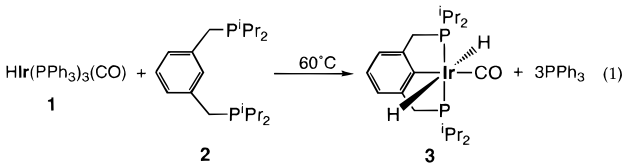
Table 1. Selected Spectral Data of Ir−PCP Complexes

	NMR, ppm			IR,[a] cm^{-1}	
compd	^{31}P{^{1}H}	^{1}H, Ir−***H***	^{13}C{^{1}H}, Ir−***C***O	ν_{CO}	ν_{Ir-H}
3[b]	57.84 (s)	−9.69 (t, $^2J_{PH}$ = 15.0 Hz)	178.63 (t, $^2J_{PC}$ = 6.8 Hz)	1978.0 (s)	1745.6 (s)
5[c]	33.65 (d, $^2J_{PP}$ = 11.9 Hz), −6.62 (t)	−9.46 (app q, $^2J_{PH}$ = 14.8 Hz)	176.57 (app q, $^2J_{PC}$ = 6.3 Hz)	2002.0 (s)	2140.9 (bm)
6[b]	66.18 (s)		196.51 (t, $^2J_{PC}$ = 7.7 Hz)	1920.0 (s)	
7[e]	31.26 (s)		178.44 (t, $^2J_{PC}$ = 5.8 Hz)	2004.0 (s)	
8[b]	51.67 (s)	−10.87 (td, $^2J_{PH}$ = 16.9 Hz, $^2J_{HH}$ = 3.2 Hz), −11.94 (td, $^2J_{PH}$ = 11.9 Hz)		1950(s)	2066.3 (bw), 1965 (w)
9[d]	34.9 (d, $^2J_{PP}$ = 12.2 Hz), −20.0 (t)	−12.04 (dt, $^2J_{PH,trans}$ = 131.1 Hz, $^2J_{PH,cis}$ = 13.1 Hz)		2012.0 (s)	2161.4 (bm)
10[b]	50.79 (s)	−18.30 (t, $^2J_{PH}$ = 11.6 Hz)	179.19 (t, $^2J_{PC}$ = 6.8 Hz)	2003.1 (s)	2197.4 (bm)
11[b]	46.53 (s)	−14.70 (td, $^2J_{PH}$ = 12.0 Hz, $^4J_{HH}$ = 3.7 Hz)	179.03 (t, $^2J_{PC}$ = 6.6 Hz)	2009.7 (s)	2120 (bw)
12[b]	42.80 (s)	−15.48 (t, $^2J_{PH}$ = 10.6 Hz)		2005.0 (s)	2193.0 (bm)

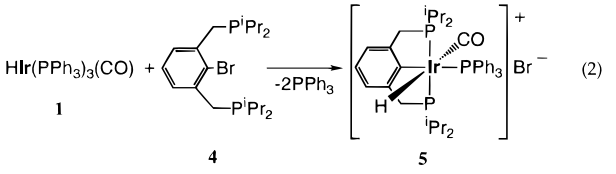
[a] All samples for IR measurements were prepared as neat films, except for the sample of **8** (benzene solution under 1 atm of hydrogen). [b] In C_6D_6. [c] In CD_2Cl_2. [d] In $CDCl_3$. [e] In acetone-d_6 (^{31}P{^{1}H} NMR), toluene-d_8 (^{13}C{^{1}H} NMR).



at 57.84 ppm, which is split into a triplet ($^2J_{PH,cis}$ = 15.0 Hz) in ^{31}P{^{1}H} hydride-coupled NMR, consistent with the presence of two equivalent hydride ligands. ^{1}H NMR and ^{13}C{^{1}H} NMR reveal that there is a symmetry plane passing through the PCP−Ir chelate core, in accordance with the *trans* arrangement of the two hydrides in **3**. The low stretching frequency of Ir−H (1745.6 cm^{-1}) is very characteristic of a *trans* H−M−H moiety and is due to the strong mutual *trans* influence of the hydride ligands.[2,9]

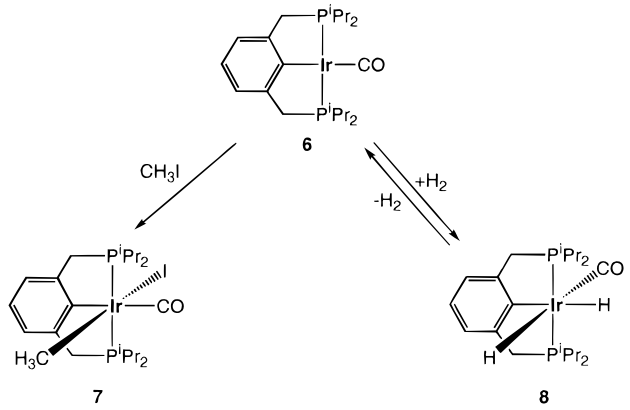
Synthesis of Iridium Complexes using a Bromo Derivative of a PCP Ligand. Reactivity of an Iridium(I) Complex. Use of bromo derivatives of PCP ligands (molecules of the type 1,3-(R_2PCH_2)$_2$-2-Br-C_6H_4) can be a useful route for the synthesis of PCP-based complexes due to facile Ar−Br bond activation.

Stirring a THF solution containing stoichiometric amounts of HIr(PPh_3)$_3$(CO) (**1**) and the ligand DIPPX-Br (**4**; DIPPX-Br, **D**i**I**so**P**ropyl**P**hosphino**X**ylene−**Br**omide (1,3-bis[(diisopropylphosphino)methyl]-2-bromobenzene) at ambient temperature for 12 h, and precipitation of the product with pentane afforded complex **5** in 84% yield (eq 2). IR and selected NMR data for **5** are given



in Table 1. The ^{31}P{^{1}H} NMR spectrum of **5** indicates that the two phosphines of the PCP ligand are *trans* to each other. ^{13}C{^{1}H} NMR and ^{1}H NMR spectra reveal that the compound does not have a symmetry plane passing through the PCP−metal chelate core. The signal of the *ipso* carbon in ^{13}C{^{1}H} NMR appears as a doublet of triplets centered at 133.07 ($^2J_{PC,trans}$ = 45.2 Hz, $^2J_{PC,cis}$ = 2.3 Hz), confirming the *trans* Ar−Ir−PPh_3 arrangement in **5**. In order to verify the ionic constitution of the compound, reaction of **5** with $TlPF_6$ was carried out. When the reaction was carried out in acetone-d_6, formation of a yellow precipitate (TlBr) was observed and no difference in the ^{31}P{^{1}H} and ^{1}H NMR spectra before and after addition of $TlPF_6$ was detected (except for the presence of the ***P***F_6^- septet in ^{31}P{^{1}H} NMR), indicating that the reaction is a simple ion exchange.

Scheme 1



The iridium(I) complex Ir(DIPPX)(CO) (**6**) was prepared in 78% yield by deprotonation of complex **5** at room temperature with KO-*t*-Bu in THF. Complex **6** is an orange oil, air-sensitive and soluble in common organic solvents. ^{1}H NMR and ^{13}C{^{1}H} NMR confirm the symmetrical geometry of **6**. The relatively low stretching frequency of the CO ligand of **6** (1920 cm^{-1}) reflects significant back-bonding from the metal to the π^* orbital of the carbonyl, as expected for terminal carbonyls in electron-rich Ir(I) complexes.

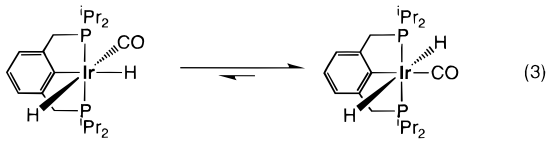
Reactions of complex **6** are presented in Scheme 1. It smoothly reacts with MeI, giving Ir(DIPPX)(CO)-(CH_3)I (**7**) in nearly quantitative yield. Complex **7** is remarkably stable and does not decompose upon heating up to 130 °C. The Ir-**CH_3** appears in the ^{1}H NMR spectrum as a triplet at 0.55 ppm ($^3J_{PH}$ = 5.0 Hz) and as a triplet at −27.18 ppm ($J_{PC,cis}$ = 4.7 Hz) in the ^{13}C-{^{1}H} NMR spectrum, as expected for methyl−Ir(III) complexes.[10] The *cis* orientation of the methyl with regard to the aromatic ring is confirmed by an NOE experiment, showing interaction between the Ir−**CH_3** protons and *one set* of Ar−C***H_2***−P and $(CH_3)_2$C***H***−P protons.

(9) Geoffroy, G. L.; Lehman, J. R. *Adv. Inorg. Chem. Radiochem.* **1977**, 189.

(10) Mann, B. E.; Taylor, B. F. *^{13}C NMR Data for Organometallic Compounds*; Academic Press: New York, 1981.

Bubbling of H_2 through a benzene solution of **6** at room temperature resulted in quantitative formation of the *cis*-dihydride **8** (Scheme 1). Complex **8** was characterized by $^{31}P\{^1H\}$ and ^1H NMR and IR. ^1H NMR reveals two hydrides oriented *cis* to each other (see Table 1), as expected for the kinetic product of dihydrogen oxidative addition. When the NMR tube, containing a benzene solution of **8** under 1 atm of H_2, is opened in a N_2 atmosphere, complex **8** loses H_2, giving the Ir(I) complex **6** quantitatively. Thus, significantly, **6** adds H_2 reversibly at ambient temperature, while other bisphosphine−iridium(I) carbonyl complexes, which do not bear a rigid tridentate chelating ligand, form stable (at room temperature) *cis*-dihydride complexes.[11]

Thermal Isomerization of the *cis*-Dihydride Complex 8 into the *trans*-Dihydride Complex 3. Two hydride ligands oriented *trans* to each other are expected to destabilize metal complexes due to their strong mutual *trans* influence. As a result, *trans*-dihydrides are rare and usually not stable, whereas many stable *cis*-dihydride late transition metal complexes are known for various ligand arrangments. Surprisingly, when it is heated at 90 °C under 35 psi of H_2 (hydrogen is needed to suppress formation of **6** from **8**), complex **8** quantitatvely converts into **3** (eq 3), clearly showing that



(3)

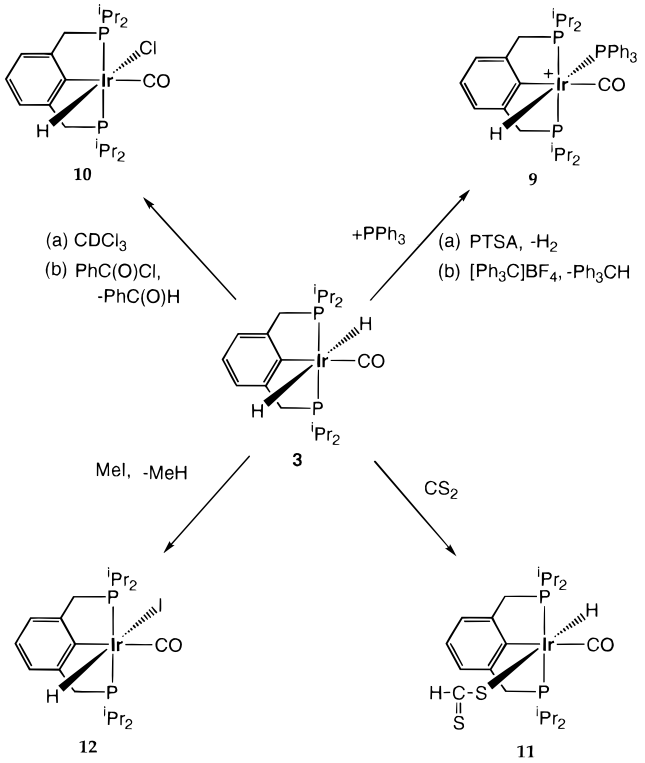
*trans-dihydride complex **3** is thermodynamically more stable than cis-dihydride complex **8**.* Assuming that $^{31}P\{^1H\}$ NMR signals can be integrated with an experimental error of about 1%, and since no *cis*-dihydride **8** was observed in $^{31}P\{^1H\}$ NMR after 18 h of heating at 90 °C, $\Delta G_{trans-cis}(363) \leq -3.3$ kcal/mol. The isomerization (eq 3) most probably involves phosphine arm opening, but an Ar−H reductive-elimination−oxidative-addition pathway is also possible. The higher thermodynamic stability of the *trans*-dihydride **3** in comparison with the *cis*-dihydride **8** contradicts the well-known *trans*-influence trend (H > Ph) and is unprecedented for hexacoordinated complexes.

Reactivity of *trans*-Ir(DIPPX)(H)$_2$(CO). The reactions of *trans*-Ir(DIPPX)(H)$_2$(CO) (**3**) are presented in Scheme 2. Selected spectral data for complexes **9**−**12** are given in Table 1.

Protonation of **3** with *p*-toluenesulfonic acid or hydride abstraction with $[Ph_3C]BF_4$ (trityl cation) at room temperature results in nearly quantitative formation of the cationic complex **9**. Formation of Ph_3CH was observed in ^1H NMR in the latter reaction. The observed large hydride−phosphorus coupling (see Table 1) in **9** is consistent with a *trans* H−Ir−PPh_3 arrangement.

Reaction of complex **3** with either benzoyl or anisoyl chloride results in formation of complex **10** and the corresponding aldehydes. The ^1H NMR spectrum of **10** exhibits a triplet at −18.30 ppm, typical for a hydride positioned *trans* to a chloride[9] and *cis* to two equivalent phosphines. The lack of a symmetry plane containing the Ir−PCP chelate core is evident from the inequivalence of the C***H***$_2$P protons. Quantitative formation of benzaldehyde and 4-methoxybenzaldehyde, respectively, was observed in ^1H NMR and confirmed by GC−MS. Complex **10** was also synthesized by keeping a $CDCl_3$ solution of **3** at room temperature for 5 days.

Scheme 2



Complex **3** reacts with CS_2.[12,13] When a THF solution of **3** containing a 20-fold excess of CS_2 is kept at room temperature for 3 days, **3** is converted into **11** in 80% yield ($^{31}P\{^1H\}$ NMR). ^1H and $^{13}C\{^1H\}$ NMR spectra of **11** reveal that there is no symmetry plane containing the Ir−PCP chelate core. The signal of the thioformyl proton appears as a doublet of triplets centered at 11.8 ppm ($^4J_{HH}$ = 3.7 Hz, $^4J_{PH}$ = 1.2 Hz) in ^1H NMR, the chemical shift and splitting pattern being distinctive of complexes in which a thioformyl group is oriented *trans* to a hydride.[13a−d] The resonance of the thioformyl carbon appears as a broad singlet at 176.86 ppm in the $^{13}C\{^1H\}$ NMR spectrum. No reaction was observed with CO_2.

Complex **3** reacts with MeI smoothly at room temperature, giving **12** in 87% yield ($^{31}P\{^1H\}$ NMR).

Discussion

***cis*- to *trans*-Dihydride Isomerization.** In the case of complexes $Pt(PR_3)_2H_2$ containing bulky phosphines

(11) For example see: (a) Johnson, C. E.; Eisenberg, R. *J. Am. Chem. Soc.* **1985**, *107*, 3148. (b) Deutsch, P. P.; Eisenberg, R. *Chem. Rev.* **1988**, *88*, 1147. (c) Eisenberg, R.; Cleary, B. P. *J. Am. Chem. Soc.* **1995**, *117*, 3510. (d) Fryzuk, M. D.; MacNeil, P.; Rettig, S. J. *Organometallics* **1986**, *5*, 2469.

(12) For the reviews on carbon disulfide activation see: (a) Butler, I. S.; Fenster, A. E. *J. Organomet. Chem.* **1974**, *66*, 161. (b) Yaneff, P. V. *Coord. Chem. Rev.* **1977**, 183. (c) Ibers, J. A. *Chem. Soc. Rev.* **1982**, 57.

(13) CS_2 activation: (a) Robinson, S. D.; Sahajpal, A. *J. Organomet. Chem.* **1975**, *99*, C65. (b) Roper, W. R.; Town, K. G. *J. Chem. Soc., Chem. Commun.* **1977**, 781. (c) Collins, T. J.; Roper, W. R. *J. Organomet. Chem.* **1978**, *159*, 73. (d) Mishra, A.; Agarwala, U. C. *Inorg. Chim. Acta* **1988**, *145*, 191. (e) Klein, D. P.; Kloster, G. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1990**, *112*, 2022. (f) Jones, W. D.; Selmeczy, A. D. *Organometallics* **1992**, *11*, 889.

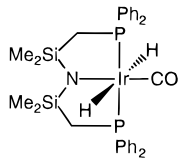
(R = *t*-Bu, Cy, *t*-Bu_2Ph, *i*-Pr_3),[2b−e] the hydride ligands are forced to be *trans* to each other, while with the less bulky PMe_3 the electronically more favorable *cis*-$Pt(PMe_3)_2H_2$ is the major isomer in solution.[2e] Thus, steric factors play a major role in the stabilization of four-coordinate platinum *trans*-dihydrides. It should be noted that in the isomerization **8** → **3** the phosphines *remain mutually trans oriented* and steric factors are unlikely to be dominant in this case. However, the geometry of **8** with the carbonyl ligand *cis* to the aryl seems sterically less favorable than that of **3** due to possible steric interaction of the CO ligand with bulky isopropyl groups.

The higher stability of complex **3** as compared with **8** cannot be attributed to back-bonding interactions involving the carbonyl ligand. On the contrary, comparison of the carbonyl stretching frequencies in **3** (1980 cm^{-1}) and **8** (1950 cm^{-1}) indicates that there is stronger electron donation to the antibonding orbitals of CO in the case of the *cis*-dihydride **8**, as expected for a carbonyl ligand oriented *trans* to a hydride.

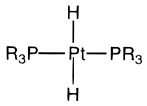
In the *cis*-dihydride complex the chelate structure may be destabilized by lengthening of the Ir-Ar bond as a result of the hydride *trans* effect. It is known that $^{31}P\{^1H\}$ NMR chemical shifts of chelate complexes are very sensitive to the chelate ring size, namely to the C−P−M angle.[14] Comparison of $^{31}P\{^1H\}$ NMR chemical shifts of **3** and **8** shows that they differ only by 6 ppm. We would expect a more dramatic effect if the chelate rings were significantly distorted.

While the reason for unexpected higher stability of the *trans*-dihydride **3** needs further clarification, it is likely to be a combination of steric and electronic factors. Both the steric bulk of the ligand *cis* to the aryl and destabilization of the chelate rings due to the *trans* effect probably contribute to the relative stability of complexes **3** and **8**.

Hydridic Reactivity of Complex 3. To the best of our knowledge only a few examples of stable late transition metal *trans*-dihydrides were reported.[2] Complex **13** is an analog of complex **3**; the reactivity of **13**



13



14

toward electrophiles was not reported.[2a] The 16-electron platinum complexes of the type **14** (R = bulky substituent) have been extensively studied.[2b−e] *trans*-$Pt(PCy_3)_2H_2$ exhibits reactivity similar to that of **3**. It reacts with CO_2 and CS_2 in noncoordinating solvents, affording the products of insertion into the Pt−H bond, the structurally characterized formate and thioformate complexes, respectively.[15] The mechanism of carbon disulfide insertion involves the addition of CS_2 to *trans*-$Pt(PCy_3)_2(H)_2$ to give a five-coordinate labile intermediate, which rapidly collapses to the final product.[15b]

Since **3** is an 18-electron chelate complex, with ligands which do not dissociate at ambient temperature (**3** is stable under 30 psi of CO for days at 45−50 °C),[16] precoordination of reagents to the metal center is not possible, unlike in the case of **14**. In the reaction of **3** with benzoyl or anisoyl chloride no decarbonylation products were observed, suggesting that oxidative addition of the acid chlorides to the metal center most probably does not take place. Thus, we propose a direct attack of the electrophiles on the hydride ligand of **3**.

True hydride-like reactivity is well-known for early transition metals,[3] anionic complexes,[4] and some polyhydrides[4c] and clusters.[5] Obviously, complex **3** belongs to none of these categories. The reactions of neutral transition-metal hydrides with strong acids or trityl cation are well-documented.[17] They result in hydride abstraction to form metal complexes with weakly coordinated anion ligands. However, the reactions of these complexes with less strong electrophiles, as in the case of **3**, have not been reported.

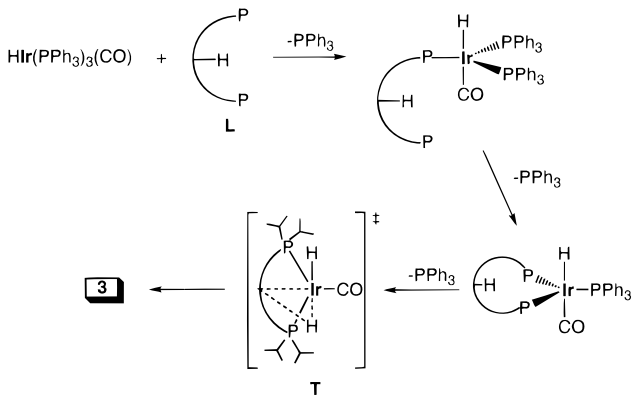
Significantly, the monohydrides (**9**−**12**), which are formed in the reactions of **3** with the electrophiles, are *inert towards the excess of the electrophilic reagents*, suggesting that the hydridic reactivity is a unique property of the *trans*-dihydride **3**. We suggest that the main reason for the hydridic reactivity of **3** is the strong mutual *trans* influence of the hydride ligands. Weakening of the normally strong Ir−H bond in the *trans*-dihydride results in its susceptibility to the electrophilic reagents. Both two-electron and single-electron (involving ion radicals) mechanisms can be operative. We are unaware of octahedral *trans*-dihydride complexes other than **3** whose reactivity was reported.

Mechanism of Formation of the *trans*-Dihydride Complex 3. H_2 addition to the Ir(I) complex **6** is reversible, as indicated by the observation that the *cis*-dihydride complex **8** eliminates dihydrogen in the absence of H_2 pressure to give the starting complex **6**. Significantly, when complex **1** is reacted with ligand **2**, the *trans*-dihydride **3** is formed in nearly quantitative yield. If the *cis*-dihydride complex **8** were generated in the reaction with a rate comparable to that of formation of **3**, we would expect to observe a significant amount of complex **6**, since under the reaction conditions (heating at 60 °C, no H_2 pressure) H_2 elimination from **8** to give complex **6** takes place immediately, whereas isomerization of **8** into **3** is significantly slower (*vide supra*). Since only 5−7% of **6** was observed in the reaction, the formation of **3** is *kinetically controlled*. Thus, interestingly, the *trans*-dihydride **3** is both the kinetic and thermodynamic product. The suggested reaction pathway explaining selective formation of **3** is presented in Scheme 3.

It is likely that in the transition state **T** the CO ligand is oriented *trans* to the aryl in order to diminish steric clashing with the bulky *i*-Pr substituents. The sterically less demanding hydride ligand bends towards the aryl, resulting in its *cis* orientation with regard to the aryl in the final product (see Scheme 3). Specific interaction of the carbonyl antibonding orbitals may also be responsible for preferential formation of complex **3**. It was

(14) Lindner, E.; Fawzi, R.; Mayer, H. A.; Elchele, K.; Hiller, W. *Organometallics* **1992**, *11*, 1033.
(15) (a) Albinati, A.; Musco, A.; Carturan, G.; Strukul, G. *Inorg. Chim. Acta* **1976**, *18*, 219. (b) Immirzi, A.; Musco, A. *Inorg. Chim. Acta* **1977**, *22*, L35.
(16) Carbonyl dissociation from complex **3** seems unlikely, since the CO ligand in **3** is strongly involved in back-bonding with the metal center, as indicated by the low CO stretching frequency (1978.0 cm^{-1}).
(17) Beck, W.; Sünkel, K. *Chem. Rev.* **1988**, *88*, 1405.

Scheme 3



suggested that the steric preferences of oxidative addition of H_2 to complexes of the type (DPPE)Ir(CO)X (X = halide, H, CN) are regulated by back-donation to CO.[18]

Nature of Facile Dihydrogen Elimination from Complex 8. The observed facile H_2 elimination from complex **8,** which seems unusual for an Ir(III) hydride complex, can be explained as follows. Theoretical calculations[19] show that during the course of H_2 oxidative addition to square-planar d^8 complexes a four-electron repulsive interaction is dominant, while upon deviation from square-planar geometry, electron density donation from the metal filled orbital into the empty H−H antibonding orbital prevails. Thus, oxidative addition of H_2 to the rigid square-planar complex **6** is disfavored, i.e. H_2 reductive elimination from **8** is favorable, whereas complexes of distorted square-planar geometry are likely to form stable dihydrides.

Summary

The *trans*-dihydride complex **3** is *both the kinetic and thermodynamic product* of the reaction of **1** with the DIPPX ligand **2**. *trans*-Ir(DIPPX)$(H)_2$(CO) (**3**) exhibits true hydride-like reactivity (it readily reacts with various electrophiles), which is due to the mutual *trans* influence of the hydride ligands.

A surprizing *cis*- into *trans*-dihydride isomerization was observed. This is unprecedented for 18-electron six-coordinate complexes. Reversible dihydrogen addition to the Ir(I)−PCP complex Ir(DIPPX)(CO) (**6**) is in accord with theory, which predicts that a rigid square-planar geometry should disfavor oxidative addition and favor reductive elimination of nonpolar substrates.

Experimental Section

General Considerations. All experiments with metal complexes were carried out under purified nitrogen in a Vacuum Atmospheres glovebox equipped with an MO 40-2 inert gas purifier. Ligand synthesis was carried out under argon. Solvent removal was performed with a high vacuum system, using precision oil vacuum pumps. All solvents were reagent grade or better. All non-deuterated solvents (except for acetone) were refluxed over sodium/benzophenone ketyl and distilled under an argon atmosphere. Acetone was dried over 4 Å molecular sieves. Deuterated solvents were used as received. Before introduction into the glovebox, all the solvents were degassed with argon. They were kept in the box over 4 Å molecular sieves. Commercially available reagents were used as received. The complex $HIr(PPh_3)_3CO$ (**1**) was prepared according to a literature procedure.[20]

^1H, ^{31}P, and ^{13}C NMR spectra were recorded at 400, 162, and 100 MHz respectively, using a Bruker AMX-400 NMR spectrometer. ^1H and ^{13}C NMR chemical shifts are reported in ppm downfield from tetramethylsilane and referenced to the residual hydrogen signal and carbon-13 signal, respectively, of the deuterated solvents. ^{31}P NMR chemical shifts are reported in ppm downfield from H_3PO_4 and referenced to an external 85% solution of phosphoric acid in D_2O. All the NMR measurements of new compounds were performed at 23 °C in C_6D_6, unless otherwise specified. Abbreviations used in the description of NMR data: app = apparent, b = broad, dist = distorted, s = singlet, d = doublet, t = triplet, quart = quartet, m = multiplet, v = virtual. IR spectra were measured with a Nicolet-510 FT-IR spectrometer, using NaCl IR cells. Field desorption (FD) mass spectrometry was performed at the University of Amsterdam using a JEOL JMS SX/SX 102A four-sector mass spectrometer, coupled to a JEOL MS-MP7000 data system; mass spectra are reported for more abundant isotope, namely ^{193}Ir. Elemental analyses were performed at the Microanalysis Laboratory of the Hebrew University of Jerusalem.

Synthesis of the DIPPX Ligand (2). To 7.12 g (296.7 mmol) of Mg turnings in 20 mL of THF was added 0.5 mL of neat 1,2-dibromoethane at room temperature. This mixture was gently heated until ethylene evolution was clearly observed; then 80 mL of THF was added, followed by a solution of 12.82 g (73.30 mmol) of 1,3-bis(chloromethyl)benzene in 910 mL of THF at room temperature. At the end of the addition the reaction mixture was stirred at room temperature for 12 h, yielding a green yellowish solution. Filteration to remove excess Mg followed by titration of this solution with *n*-butanol using *o*-phenanthroline as an indicator revealed formation of the desired 1,3-bis[(chloromagnesio)methyl]benzene product in 96% yield. A THF solution (1000 mL) of the di-Grignard (70.4 mmol) was added at 0 °C to a solution of 24 g (157 mmol) of ClP-*i*-Pr_2 in 500 mL of THF. At the end of the addition, the reaction mixture was warmed to room temperature and was stirred for an additional 20 h. The solvent was removed by vacuum, and the waxy residue was extracted with 3 × 500 mL of ether. The ether was distilled at atmospheric pressure, and the residue was fractionated under high vacuum to give 12.23 g (51%) of the pure product. Bp: 105 °C (2×10^{-3} mmHg). $^{31}P\{^1H\}$ NMR: 10.23 (s). ^1H NMR: 7.37 (bs, 1H, ***Ar***), 7.11 (m, 3H, ***Ar***), 2.60 (bs, 4H, 2 Ar−C***H***$_2$−P), 1.6 (m, 4H, 2 $(CH_3)_2C$***H***−P), 0.99 (dd, $^3J_{PH}$ = 0.4 Hz, $^3J_{HH}$ = 7.1 Hz, 12H, 2 $(CH_3)_2$CH−P), 0.96 (dd, $^3J_{PH}$ = 2.2 Hz, $^3J_{HH}$ = 7.1 Hz, 12H, 2 $(CH_3)_2$CH−P).

Preparation of *trans*-Ir(DIPPX)$(H)_2$(CO) (3). A solution of DIPPX (**2**; 30 mg, 0.089 mmol) in 3 mL of THF was added to a THF solution (7 mL) of $HIr(PPh_3)_3CO$ (**1**; 89 mg, 0.088 mmol). The resulting yellow solution was heated at 60−62 °C in a closed vessel for 2 h with stirring, upon which it turned light orange. *trans*-Ir(DIPPX)$(H)_2$(CO) was formed in 93% yield ($^{31}P\{^1H\}$ NMR). A small amount of Ir(DIPPX)CO (**6**; 7%) was also formed. When benzene is used as a solvent instead of THF, **3** is formed in 95% yield. All attempts to separate **3** from PPh_3 by crystallization or chromatography on alumina or silica and by use of $PdCl_2(CH_3CN)_2$ as a phosphine sponge did not result in complete PPh_3 removal. The compound is very soluble in common organic solvents and is air-stable.

Characterization of 3. PPh_3 signals are excluded from the NMR data. $^{31}P\{^1H\}$ NMR: δ 57.84 (s). $^{31}P\{^1H\}$ hydride-coupled NMR: δ 57.84 (t, $^2J_{PH,cis}$ = 15.0 Hz). ^1H NMR: δ 6.99 (m, 2H, H_{meta}, Ir−***Ar***), 6.91 (m, 1H, H_{para}, Ir−***Ar***), 3.13 (vt,

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(20) Wilkinson, G. *Inorg. Synth.* **1972**, *13*, 126.

$J_{PH,virt}$ = 4.1 Hz, 4H, 2 Ar−C***H***$_2$−P), 1.72 (m, 4H, 4 $(CH_3)_2$C***H***−P), 1.1 (app quart, J = 7.4 Hz, 12H, 2 (C***H***$_3)_2$CH−P), 0.93 (app quart, J = 7.1 Hz, 12H, 2 (C***H***$_3)_2$CH−P), −9.69 (t, $^2J_{PH,cis}$ = 15.0 Hz, 2H, ***H***−Ir−***H***). ^{13}C{^{1}H} NMR: δ 178.63 (t, $^2J_{PC,cis}$ = 6.8 Hz, Ir−***C***O), 151.62 (t, J_{PC} = 3.2 Hz, Ir−***Ar***), 147.23 (t, J_{PC} = 8.8 Hz, Ir−***Ar***), 122.94 (bs, C_{para}, Ir−***Ar***), 120.83 (t, J_{PC} = 8.3 Hz, C_{meta}, Ir−***Ar***), 41.23 (vt, $J_{PC,virt}$ = 17.6 Hz, Ar−***C***H$_2$−P), 25.85 (vt, $J_{PC,virt}$ = 15.9 Hz, $(CH_3)_2$***C***H−P), 19.57 (vt, $J_{PC,virt}$ = 1.5 Hz, (***C***H$_3)_2$CH−P), 18.14 (s, (***C***H$_3)_2$CH−P). Assignment of ^{13}C{^{1}H} NMR signals is confirmed by ^{13}C DEPT 135. IR (film): 1978.0 cm^{-1} (s), ν_{CO}; 1745.6 cm^{-1} (s), ν_{H-Ir-H}. IR (C_6D_6): 1980.0 cm^{-1} (s), ν_{CO}; 1750 cm^{-1} (s), ν_{H-Ir-H}. FDMS: m/z 560, M$^+$.

Synthesis of the DIPPX-Br Ligand (4). A mixture of diisopropylphosphine (0.829 g, 7.97 mmol) and 1,3-bis(bromomethyl)-2-bromobenzene[21] (1.2 g, 3.53 mmol) in degassed acetone (5 mL) was heated under reflux with stirring for 40 min under an argon atmosphere, and then the solvent was evaporated. The solid was washed with ether to remove unreacted starting material. The resulting diphosphonium salt was dissolved in distilled degassed water (10 mL) and treated with a solution of sodium acetate (4 g, 48 mmol) in distilled degassed water (10 mL). The precipitated diphosphine was extracted with ether (3 × 50 mL) and dried over Na_2SO_4, and the ether solution was filtered via sinter tube under argon pressure. The solvent was evaporated under vacuum, giving 0.800 g (65.9%) of the ligand **4** as a white solid. ^{31}P{^{1}H} NMR (C_6D_6): δ 6.65 (s). ^{1}H NMR (C_6D_6): δ 7.35 (bd (dist), $^2J_{HH}$ = 7.4 Hz, 2H, ***Ar***), 7.05 (bt (dist), 1H, ***Ar***), 3.06 (d, $^2J_{HP}$ = 1.7 Hz, 4H, 2 Ar−C***H***$_2$−P), 1.76 (m, 4H, 2 $(CH_3)_2$C***H***−P), 1.11 (m, 24H, 4 (C***H***$_3)_2$CH−P).

Preparation of [Ir(DIPPX)(PPh$_3$)(H)(CO)]Br (5). A solution of DIPPX (**2**; 62 mg, 0.149 mmol) in 2 mL of THF was added dropwise to a THF solution (4 mL) of HIr(PPh$_3)_3$CO (**1**; 150 mg, 0.145 mmol). The mixture was stirred for 24 h at room temperature until its color turned from deep yellow to greenish. The product was precipitated with 8 mL of cold pentane. The white precipitate was collected by filtration, washed with pentane (3 × 2 mL), and dried under vacuum, yielding 112 mg (84%) of **5**. The compound is soluble in polar organic solvents such as acetone, THF, chloroform, methylene chloride and insoluble in pentane, benzene, and toluene.

Characterization of 5. ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 33.65 (d, $^2J_{PP,cis}$ = 11.9 Hz, 2P, *trans* ***P***−Ir−***P***), −6.62 (t, 1P, Ir−***P***Ph$_3$). ^{1}H NMR (CD_2Cl_2): δ 7.70 (m, 6H, Ir−P***Ph$_3$***), 7.53 (m, 9H, Ir−P***Ph$_3$***), 7.12 (bd (dist), $^2J_{HH}$ = 7.4 Hz, 2H, H_{meta}, Ir−***Ar***), 7.02 (bt (dist), 1H, H_{para}, Ir−***Ar***), 3.48 (m, unresolved AB pattern, 4H, 2 Ar−C***H***$_2$−P), 1.69 (m, 2H, 2 $(CH_3)_2$C***H***−P), 1.46 (m, 2H, $(CH_3)_2$C***H***−P), 0.88 (app quart, J = 7.1 Hz, 6H, (C***H***$_3)_2$-CH−P), 0.77 (m, 18H, 3 (C***H***$_3)_2$CH−P), −9.46 (app quart, $^2J_{PH}$ = 14.8 Hz, 1H, Ir−***H***). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 176.57 (app quart, $^2J_{PC,cis}$ = 6.3 Hz, Ir−***C***O), 144.69 (td, J_{PC} = 4.9 Hz, J_{PC} = 2.3 Hz), 138.91 (d, $^2J_{PC}$ = 71.3 Hz, C_{ipso}, Ir−P***Ph$_3$***), 134.98 (d, J_{PC} = 10.7 Hz), 133.07 (dt, $^2J_{PC,trans}$ = 45.2 Hz, $^2J_{PC,cis}$ = 2.3 Hz, C_{ipso}, ***Ar***−Ir), 132.32 (d, J_{PC} = 2.3 Hz), 129.2 (d, J_{PC} = 9.9 Hz), 126.92 (s), 122.83 (td, J_{PC} = 7.3 Hz, J_{PC} = 3.2 Hz), 39.52 (vtd, $J_{PC,virt}$ = 18.3 Hz, $^3J_{PC}$ = 7.2 Hz, Ar−***C***H$_2$−P), 26.37 (vt, $J_{PC,virt}$ = 13.7 Hz, $(CH_3)_2$***C***H−P), 25.70 (vt, $J_{PC,virt}$ = 15.6 Hz, $(CH_3)_2$***C***H−P), 19.44 (s, (***C***H$_3)_2$CH−P), 19.35 (s, (***C***H$_3)_2$CH−P), 17.90 (bs, (***C***H$_3)_2$CH−P), 17.46 (vt, $J_{PC,virt}$ = 1.1 Hz, (***C***H$_3)_2$-CH−P). Assignment of ^{13}C{^{1}H} NMR signals is confirmed by ^{13}C DEPT 135. IR (film): 2140.9 cm^{-1} (bm), ν_{Ir-H}; 2002.0 cm^{-1} (s), ν_{CO}. Anal. Calcd: C, 52.00; H, 5.71. Found: C, 52.30; H, 6.01. FD-MS: m/z 821, [Ir(DIPPX)(PPh$_3$)(H)(CO)]$^+$.

Reaction of 5 with TlPF$_6$. A solution of TlPF$_6$ (4 mg, 0.0115 mmol) in acetone-d_6 (0.5 mL) was added to a solution of [Ir(DIPPX)(PPh$_3$)(H)(CO)]Br (**5**; 10 mg, 0.0111 mmol) in 0.5 mL of acetone-d_6, resulting in immediate precipitation. The mixture was filtered; ^{31}P{^{1}H} and ^{1}H NMR revealed no difference in the spectra before and after the addition of TlPF$_6$, except for the ***P***F$_6^-$ septet in ^{31}P{^{1}H} NMR.

Preparation of Ir(DIPPX)(CO) (6). A solution of KO-*t*-Bu (12 mg, 0.107 mmol) in 3 mL of THF was added to a solution of [Ir(DIPPX)(H)(PPh$_3$)(CO)]Br (**5**; 48 mg, 0.053 mmol) in 3 mL of THF. After 2 h of stirring at room temperature the reaction mixture turned orange. The solvent was evaporated, and the residue was extracted with pentane. The orange pentane extract was filtered, and the solvent was evaporated, resulting in 28 mg of orange oil, which appeared to be a mixture of **6** and PPh$_3$ (^{31}P{^{1}H} NMR; **6**: PPh$_3$ = 1:1). The estimated yield of **6** is 78%. The product is very sensitive to air and is very soluble in common organic solvents. It was not separated from PPh$_3$.

Characterization of 6. PPh$_3$ signals are excluded from the NMR data. ^{31}P{^{1}H} NMR: δ 66.18 (s). ^{1}H NMR: δ 7.28 (bd (dist), $^2J_{HH}$ = 7.4 Hz, 2H, H_{meta}, Ir−***Ar***), 7.17 (bt (dist), 1H, H_{para}, Ir−***Ar***), 3.20 (vt, $J_{PH,virt}$ = 4.0 Hz, 4H, 2 Ar−C***H***$_2$−P), 2.02 (m, 4H, 4 $(CH_3)_2$C***H***−P), 1.20 (app quart, J = 7.5 Hz, 12H, 2 (C***H***$_3)_2$CH−P), 0.97 (app quart, J = 7.1 Hz, 12H, 2 (C***H***$_3)_2$-CH−P). ^{13}C{^{1}H} NMR: δ 196.51 (t, $^2J_{PC,cis}$ = 7.7 Hz, Ir−***C***O), 154.34 (t, J_{PC} = 11.4 Hz, Ir−***Ar***), 125.75 (s, Ir−***Ar***), 120.64 (t, J_{PC} = 8.7 Hz, Ir−***Ar***), 38.94 (vt, $J_{PC,virt}$ = 15.7 Hz, Ar−***C***H$_2$−P), 26.81 (vt, $J_{PC,virt}$ = 14.5 Hz, $(CH_3)_2$***C***H−P), 19.53 (vt, $J_{PC,virt}$ = 2.2 Hz, (***C***H$_3)_2$CH−P), 18.81 (s, (***C***H$_3)_2$CH−P). Assignment of ^{13}C{^{1}H} NMR signals is confirmed by ^{13}C DEPT 135. IR (film): 1920.0 cm^{-1} (s), ν_{CO}.

Reaction of Complex 6 with MeI. Formation of Ir(DIPPX)(CO)(CH$_3$)I (7). To 2 mL of a benzene solution of Ir(DIPPX)CO (**6**; 19 mg of a mixture, **6**:PPh$_3$ = 1:1) was added 3 μL of CH$_3$I. After 10 min of stirring at room temperature the initial orange color of the mixture almost disappeared and a white precipitate formed (the phosphonium salt [CH$_3$PPh$_3$]I, identified by ^{31}P{^{1}H} and ^{1}H NMR). The mixture was filtered and the solvent was evaporated under vacuum, giving 16 mg (98.8%) of pure **7** as a white solid. The compound is soluble in benzene and toluene and in polar organic solvents such as acetone, THF, chloroform, and methylene chloride and is moderately soluble in pentane.

Characterization of 7. ^{31}P{^{1}H} NMR (acetone-d_6): δ 31.26 (s). ^{1}H NMR (acetone-d_6): δ 7.04 (bd (dist), $^2J_{HH}$ = 7.4 Hz, 2H, H_{meta}, Ir−***Ar***), 6.80 (bt (dist), 1H, H_{para}, Ir−***Ar***), 3.86 (dvt, the left part of an AB pattern, $^2J_{HH}$ = 16.0 Hz, $J_{PH,virt}$ = 4.4 Hz, 2H, Ar−C***H***$_2$−P), 3.70 (dvt, the right part of an AB pattern, $J_{PH,virt}$ = 4.1 Hz, 2H, Ar−C***H***$_2$−P), 3.27 (m, 2H, 2 $(CH_3)_2$C***H***−P), 2.56 (m, 2H, 2 $(CH_3)_2$C***H***−P), 1.34 (m, 24H, 4 (C***H***$_3)_2$CH−P), 0.55 (t, $^3J_{PH}$ = 5.0 Hz, 3H, C***H***$_3$−Ir). ^{1}H NMR (toluene-d_8; selected signals): δ 3.68 (dvt, the left part of an AB pattern, 2H, Ar−C***H***$_2$−P), 3.30 (dvt, the right part of an AB pattern, overlapped with the signal at 3.27, Ar−C***H***$_2$−P), 3.27 (m, overall integration with the signal at 3.30 4H, $(CH_3)_2$C***H***−P), 2.14 (m, overlapped with the signal of toluene-d_8 methyl group, $(CH_3)_2$C***H***−P), 0.54 (t, $^3J_{PH}$ = 5.0 Hz, 3H, C***H***$_3$−Ir). The assignment of ^{1}H NMR signals is confirmed by ^{1}H{^{31}P} NMR. ^{13}C{^{1}H} NMR (toluene-d_8): δ 178.44 (t, $^2J_{PC,cis}$ = 5.8 Hz, Ir−***C***O), 158.08 (bs, ***Ar***−Ir), 147.12 (t, J_{PC} = 7.8 Hz, ***Ar***−Ir), 125.16 (s, ***Ar***−Ir), 121.98 (t, J_{PC} = 7.8 Hz, ***Ar***−Ir), 40.11 (vt, $J_{PC,virt}$ = 17.5 Hz, Ar−***C***H$_2$−P), 28.33 (vt, $J_{PC,virt}$ = 15.0 Hz, $(CH_3)_2$***C***H−P), 22.32 (vt, $J_{PC,virt}$ = 13.1 Hz, $(CH_3)_2$***C***H−P), 20.11 (s, (***C***H$_3)_2$-CH−P), 19.73 (s, (***C***H$_3)_2$CH−P), 19.68 (bs, (***C***H$_3)_2$CH−P), 19.16 (s, (***C***H$_3)_2$CH−P), −27.18 (t, $J_{PC,cis}$ = 4.7 Hz, ***C***H$_3$−Ir). IR (film): 2004.0 cm^{-1} (s), ν_{CO}. Anal. Calcd: C, 37.77; H, 5.47. Found: C, 39.25; H, 5.63.

^{1}H NOE Difference Experiment (toluene-d_8). When the CH$_3$-Ir group protons of **10** were selectively irradiated, selective enhancement of the methylene proton signal at 3.30 ppm and the methyne proton signal at 2.14 ppm was observed.

Reaction of Complex 6 with H$_2$. Reversible Formation of *cis*-Ir(DIPPX)(H)$_2$(CO) (8). Complex **8** was formed quantitatively within 10 min upon bubbling of hydrogen gas through 0.6 mL of a C_6D_6 solution of Ir(DIPPX)CO (**6**; 10 mg

(21) Liou, S.-Y. Ph.D. Thesis, The Weizmann Institute of Science, Rehovot, Israel 1996.

of a mixture, **6**:PPh_3 = 1:1) in a closed vessel (septum-capped NMR tube). A color change from orange to light yellow was observed. $^{31}P\{^1H\}$ and ^1H NMR of the solution indicated quantitative formation of complex **8**. Upon opening of the tube in a glovebox and standing for 15 min at room temperature the solution color turned from light yellow to orange. $^{31}P\{^1H\}$ and ^1H NMR revealed quantitative formation of Ir(DIPPX)-CO (**6**).

Characterization of 8. PPh_3 signals are excluded from the NMR data. $^{31}P\{^1H\}$ NMR: δ 51.67 (s). ^1H NMR: δ 7.12 (m, 3H, Ir−***Ar***), 4.46 (s, H_2), 3.22 (m, unresolved AB pattern, 4H, Ar−C***H***$_2$−P), 1.91 (m, 2H, 2 $(CH_3)_2$C***H***−P), 1.60 (m, 2H, 2 $(CH_3)_2$C***H***−P), 1.03 (m, 18H, 3 (C***H***$_3)_2$CH−P), 0.84 (app quart, J = 7.0 Hz, 6H, (C***H***$_3)_2$CH−P), −10.87 (td, $^2J_{PH,cis}$ = 16.9 Hz, $^2J_{HH,cis}$ = 3.2 Hz, 1H, Ir−***H***), −11.94 (td, $^2J_{PH,cis}$ = 11.9 Hz, 1H, Ir−***H***). IR (C_6H_6, 1 atm of H_2): 2066.3 cm^{-1} (bw), ν_{Ir-H}; 1965.0 cm^{-1} (w), ν_{Ir-H}; 1950.0 cm^{-1} (s), ν_{CO}.

Isomerization of 8 into 3. Heating of complex **8** at 90 °C in a 5 mm high-pressure NMR tube for 18 h under 35 psi of H_2 results in quantitatve formation of **3** ($^{31}P\{^1H\}$ and ^1H NMR followup).

Reaction of 3 with PTSA (*p*-Toluenesulfonic Acid). Formation of [Ir(DIPPX)(PPh_3)(H)(CO)]$^+$ (9). A 2 mL portion of a THF solution of *trans*-Ir(DIPPX)$(H)_2$(CO) (**3**; 20 mg of a mixture, **3**:PPh_3 = 1:3) was added to 2 mL of a THF solution of PTSA (7-fold excess), and the mixture was stirred at room temperature for 2 h. The product was precipitated with 3 mL of pentane, washed with pentane (3 × 2 mL), and dried under vacuum, giving 7 mg (53% yield) of the white product **9**. The product is soluble in polar organic solvents ($CHCl_3$, CH_2Cl_2, THF) and insoluble in benzene and toluene.

Reaction of 3 with Trityl Cation ($[Ph_3C]BF_4$). Formation of Complex 9 and Ph_3CH. A 2 mL portion of a CH_2Cl_2 solution of *trans*-Ir(DIPPX)$(H)_2$(CO) (**3**; 20 mg of a mixture, **3**:PPh_3 = 1:3) was added to 2 mL of a CH_2Cl_2 solution of $[Ph_3C]$-BF_4 (2-fold excess), and the mixture was stirred at room temperature for 2 h. Then the product was precipitated with 4 mL of pentane, washed with pentane (3 × 2 mL), and dried under vacuum, giving 8 mg (estimated yield 60%) of the white product **9**. Formation of Ph_3CH was observed in ^1H NMR.

Characterization of 9. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 34.9 (d, $^2J_{PP,cis}$ = 12.2 Hz, 2P, trans ***P***−Ir−***P***), −20.0 (t, 1P, Ir−***P***Ph_3). ^1H NMR ($CDCl_3$): δ 7.69 (m, 3H, Ir−*P****Ph****$_3$*), 7.51 (m, 6H, Ir−*P****Ph****$_3$*), 7.37 (m, 6H, Ir−*P****Ph****$_3$*), 7.25 (bt (dist), $^2J_{HH}$ = 7.4 Hz, 1H, H_{para}, Ir−***Ar***), 7.18 (bd (dist), 2H, H_{meta}, Ir−***Ar***), 5.50 (s, Ph_3C***H***, when $[Ph_3C]BF_4$ is used), 3.48 (dvt, the left part of an AB pattern, $^2J_{HH}$ = 17.2 Hz, $J_{PH,virt}$ = 4.8 Hz, 2H, Ar−C***H***$_2$−P), 2.57 (m, 2H, 2 $(CH_3)_2$C***H***−P), 2.38 (dvt, the right part of an AB pattern, $J_{PH,virt}$ = 4.4 Hz, 2H, Ar−C***H***$_2$−P), 1.49 (m, 8H, 2 $(CH_3)_2$C***H***−P and (C***H***$_3)_2$CH−P), 1.38 (app quart, J = 7.4 Hz, 6H, (C***H***$_3)_2$CH−P), 1.17 (app quart, J = 7.2 Hz, 6H, (C***H***$_3)_2$-CH−P), 0.90 (app quart, J = 7.3 Hz, 6H, (C***H***$_3)_2$CH−P), −12.04 (dt, $^2J_{PH,trans}$ = 131.1 Hz, $^2J_{PH,cis}$ = 13.1 Hz, 1H, *trans* ***H***−Ir−PPh_3). IR (film): 2161.4 cm^{-1} (bm) ν_{Ir-H}; 2012.0 cm^{-1} (s), ν_{CO}.

Reaction of 3 with $CDCl_3$. Formation of Ir(DIPPX)-(H)(CO)Cl (10). Keeping a solution of *trans*-Ir(DIPPX)$(H)_2$-(CO) (**3**; 50 mg of a mixture, **3**:PPh_3 = 1:3) in 0.6 mL of $CDCl_3$ at room temperature for 5 days resulted in a clean quantitative conversion of **3** into **10**. Complex **10** was precipitated with 3 mL of pentane and washed with pentane (3 × 1 mL), yielding 19 mg (86.1%) of complex **10** as a white precipitate.

Characterization of 10. $^{31}P\{^1H\}$ NMR: δ 50.79 (s). ^1H NMR: δ 7.05 (m, 3H, Ir−***Ar***), 3.42 (dvt, the left part of an AB pattern, $^2J_{HH}$ = 16.4 Hz, $J_{PH,virt}$ = 4.4 Hz, 2H, Ar−C***H***$_2$−P), 3.01 (dvt, the right part of an AB pattern, $J_{PH,virt}$ = 4.3 Hz, 2H, Ar−C***H***$_2$−P), 2.86 (m, 2H, 2 $(CH_3)_2$C***H***−P), 1.67 (m, 2H, 2 $(CH_3)_2$C***H***−P), 1.33 (app quart, J = 7.4 Hz, 6H, (C***H***$_3)_2$CH−P), 1.08 (app quart, J = 7.2 Hz, 6H, (C***H***$_3)_2$CH−P), 0.91 (app quart, J = 7.3 Hz, 6H, (C***H***$_3)_2$CH−P), 0.68 (app quart, J = 7.0 Hz, 6H, (C***H***$_3)_2$CH−P), −18.30 (t, $^2J_{PH,cis}$ = 11.6 Hz, 1H, trans−***H***−Ir−Cl). $^{13}C\{^1H\}$ NMR: δ 179.19 (t, $^2J_{PC,cis}$ = 6.8 Hz, Ir−***C***O), 156.66 (t, J_{PC} = 2.1 Hz, ***Ar***−Ir), 148.54 (t, J_{PC} = 8.4 Hz, ***Ar***−Ir), 124.95 (s, ***Ar***−Ir), 121.52 (t, J_{PC} = 8.3 Hz, ***Ar***−Ir), 40.01 (vt, $J_{PC,virt}$ = 17.6 Hz, Ar−***C***H_2−P), 25.47 (vt, $J_{PC,virt}$ = 14.8 Hz, $(CH_3)_2$***C***H−P), 24.39 (vt, $J_{PC,virt}$ = 15.3 Hz, $(CH_3)_2$***C***H−P), 20.32 (vt, $J_{PC,virt}$ = 1.5 Hz, (***C***$H_3)_2$CH−P), 19.63 (bs, (***C***$H_3)_2$CH−P), 18.70 (s, (***C***$H_3)_2$CH−P), 17.56 (bs, (***C***$H_3)_2$-CH−P). IR (film): 2197.4 cm^{-1} (bm), ν_{Ir-H}; 2003.1 cm^{-1} (s) ν_{CO}. FD-MS m/z 594, M^+

Reaction of 3 with Benzoyl Chloride. Formation of Complex 10 and Benzaldehyde. Benzoyl chloride (3 μL, 0.026 mmol, 1.7-fold excess) was added to a benzene-d_6 solution of *trans*-Ir(DIPPX)$(H)_2$(CO) (**3**; 20 mg of a mixture, **3**:PPh_3 = 1:3). After the mixture was kept at room temperature for 4 h, quantitative formation of **3** was observed ($^{31}P\{^1H\}$ NMR). Quantitative formation of benzaldehyde was observed in ^1H NMR (a known quantity of 4-methoxybenzaldehyde was added to the reaction mixture as an internal standard). Formation of benzaldehyde was also detected by GC−MS.

Reaction of 3 with Anisoyl Chloride. Formation of Complex 10 and 4-Methoxybenzylaldehyde. Anisoyl chloride (5 mg, 0.029 mmol, 2-fold excess) was added to a benzene-d_6 solution of *trans*-Ir(DIPPX)$(H)_2$(CO) (**3**; 20 mg of a mixture, **3**:PPh_3 = 1:3). After the mixture was kept at room temperature for 4 h, formation of **5** and 4-methoxybenzylaldehyde was observed in quantitative yield by ^1H NMR (a known quantity of benzaldehyde was added to the reaction mixture, and the integration of aldehyde protons was compared).

Reaction of Complex 3 with CS_2. Formation of Ir-(DIPPX)(H)(HC(S)S)CO (11). CS_2 (0.1 mL, 79 mg, 1.039 mmol) was added to a THF solution (2 mL) of *trans*-Ir(DIPPX)-$(H)_2$(CO) (**3**; 80 mg of a mixture, **3**:PPh_3 = 1:3), resulting in a yellow solution. After the mixture was kept for 3 days at room temperature, the solution turned brown. The solvent was evaporated under vacuum, giving complex **6** as a brown oil in 80% yield ($^{31}P\{^1H\}$ NMR). The product is very soluble in common organic solvents. It was not separated from PPh_3.

Characterization of 11. PPh_3 signals are excluded from the NMR data. $^{31}P\{^1H\}$ NMR: δ 46.53 (s). ^1H NMR: δ 11.8 (dt, $^4J_{HH}$ = 3.7 Hz, $^4J_{PH}$ = 1.2 Hz, 1H, ***H***C(S)S−Ir), the signals of the product aromatic protons are overlapped with the signals of PPh_3, 3.19 (dvt, the left part of an AB pattern, $^2J_{HH}$ = 16.6 Hz, $J_{PH,virt}$ = 4.2 Hz, 2H, Ar−C***H***$_2$−P), 2.88 (dvt, the right part of an AB pattern, $J_{PH,virt}$ = 4.3 Hz, 2H, Ar−C***H***$_2$−P), 2.32 (m, 2H, 2 $(CH_3)_2$C***H***−P), 1.60 (m, 2H, 2 $(CH_3)_2$C***H***−P), 1.16 (app quart, J = 7.3 Hz, 6H, (C***H***$_3)_2$CH−P), 0.98 (app quart, J = 6.9 Hz, 6H, (C***H***$_3)_2$CH−P), 0.84 (app quart, J = 7.1 Hz, 6H, (C***H***$_3)_2$-CH−P), 0.67 (app quart, J = 7.0 Hz, 6H, (C***H***$_3)_2$CH−P), −14.70 (td, $^2J_{PH}$ = 12.0 Hz, $^4J_{HH}$ = 3.7 Hz, 1H, Ir−***H***). Assignment of the signals in ^1H NMR is confirmed by $^1H\{^{31}P\}$ NMR. $^{13}C\{^1H\}$ NMR: δ 179.03 (t, $^2J_{PC,cis}$ = 6.6 Hz, Ir−***C***O), 176.86 (bs, H***C***(S)S−Ir), 149.22 (bs, ***Ar***−Ir), 148.64 (t, J_{PC} = 8.0 Hz, ***Ar***−Ir), 124.98 (s, ***Ar***−Ir), 121.67 (t, J_{PC} = 8.3 Hz, ***Ar***−Ir), 40.52 (vt, $J_{PC,virt}$ = 17.6 Hz, Ar−***C***H_2−P), 26.77 (vt, $J_{PC,virt}$ = 14.9 Hz, $(CH_3)_2$***C***H−P), 24.74 (vt, $J_{PC,virt}$ = 15.9 Hz, $(CH_3)_2$***C***H−P), 20.18 (bs, (***C***$H_3)_2$CH−P), 20.06 (vt, $J_{PC,virt}$ = 1.5 Hz, (***C***$H_3)_2$-CH−P), 18.78(s, (***C***$H_3)_2$CH−P), 17.77 (bs, (***C***$H_3)_2$CH−P). Assignment of $^{13}C\{^1H\}$ NMR signals is confirmed by ^{13}C DEPT 135. IR (film): 2120.0 cm^{-1} (bw), ν_{Ir-H}, 2009.7 cm^{-1} (s), ν_{CO}; 1220 cm^{-1} (bm), 1025 cm^{-1} (bs). FDMS: m/z 636, M^+.

Reaction of Complex 3 with MeI. Formation of Ir-(DIPPX)(H)(CO)I (12). MeI (10 μL, 0.161 mmol) was added to a benzene solution of *trans*-Ir(DIPPX)$(H)_2$(CO) (**3**; 30 mg of a mixture, **3**:PPh_3 = 1:3), resulting in formation of a white precipitate (the phosphonium salt $[CH_3PPh_3]I$, identified by $^{31}P\{^1H\}$ and ^1H NMR). The solvent was evaporated, and the residue was extracted with toluene. The extract was filtered, and the solvents were evaporated under vacuum, yielding a greenish residue. $^{31}P\{^1H\}$ NMR of the residue revealed formation of Ir(DIPPX)(H)(CO)I (**12**) in 85% yield (contaminated with traces of unidentified complexes).

Characterization of 12. $^{31}P\{^1H\}$ NMR: δ 42.80 (s). ^1H NMR: δ 7.31 (bs, 2H, H_{meta}, Ir−***Ar***), 7.22 (m, 1H, H_{para}, Ir−

Ar), 3.58 (dvt, the left part of an AB pattern, $^2J_{HH} = 16.5$ Hz, $J_{PH,virt} = 4.7$ Hz, 2H, Ar−C***H***$_2$−P), 3.31 (m, overlapped with the signal at 3.26, 2H, $(CH_3)_2$C***H***−P), 3.26 (dvt, the right part of an AB pattern, $J_{PH,virt} = 4.3$ Hz, overall integration with the signal at 3.31 4H, Ar−C***H***$_2$−P), 1.79 (m, 2H, 2 $(CH_3)_2$C***H***−P), 1.56 (app quart, $J = 7.4$ Hz, 6H, (C***H***$_3$)$_2$CH−P), 1.05 (m, 12H, 2 (C***H***$_3$)$_2$CH−P), 0.79 (app quart, J = 7.2 Hz, 6H, (C***H***$_3$)$_2$-CH−P), −15.48 (t, $^2J_{PH,cis} = 10.6$ Hz, 1H, trans ***H***−Ir−I). IR (film): 2193.0 cm^{-1} (bm), ν_{Ir-H}; 2005.0 cm^{-1} (s), ν_{CO}. FD−MS: m/z 686, M^+.

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