containing 0.55 mol of dimethyldimethoxysilane (or diphenyldimethoxysilane or diphenylmethoxychlorosilane) under a nitrogen atmosphere. After the addition was completed, the reaction mixture was stirred at room temperature for 1 h and then refluxed for 5 h. It was then cooled by an ice-water bath. Addition of saturated ammonium chloride to the ice-cooled reaction mixture was followed by extraction with water. The ether layer was separated and dried over anhydrous Na_2SO_4. After filtration from the drying agent and careful removal of ether, the residue was distilled.

The pure compounds were collected by VPC using a 15% SF96 column for diphenyl-*sec*-butylmethoxysilane and diphenylcyclopentylmethoxysilane and a 30% FFAP column for dimethylcyclopentylmethoxysilane.

Diphenyl-*sec*-butylmethoxysilane: yield 52.5% (based on diphenylmethoxychlorosilane); ^1H NMR ($CDCl_3$) δ 7.62–7.34 (m, 10), 3.48 (s, 3), 1.81–1.88 (m, 9); ^{13}C NMR ($CDCl_3$) δ 135.18, 129.17, 127.76 (phenyl carbon), 51.54 (OCH_3), 24.02 (CH_2), 20.12 (CH), 13.35 (CH_3), 13.13 (CH_3).

Anal. Calcd for $C_{17}H_{22}OSi$: C, 76.54; H, 7.85. Found: C, 76.57; H, 7.93.

Cyclopentyldiphenylmethoxysilane: yield 42.8% (based on diphenyldimethoxysilane); ^1H NMR ($CDCl_3$) δ 7.59–7.38 (m, 10, phenyl), 3.52 (s, 3, OCH_3), 1.99–1.51 (m, 9); ^{13}C NMR ($CDCl_3$) δ 135.13, 129.71, 217.76 (phenyl carbon), 51.59 (OCH_3), 27.76, 27.00, 23.91 (cyclopentyl carbon).

Anal. Calcd for $C_{18}H_{22}OSi$: C, 75.50; H, 8.20. Found: C, 75.60; H, 8.26.

Cyclopentyldimethylmethoxysilane: yield 48.7% (based on dimethyldimethoxysilane); ^1H NMR ($CDCl_3$) δ 3.43 (s, 3, OCH_3), 1.92–1.00 (m, 9), 0.06 (s, 6, CH_3Si); ^{13}C NMR ($CDCl_3$) δ 50.56 (OCH_3) 27.43, 27.00, 25.86 (cyclopentyl carbon), −3.82 (CH_3Si).

Anal. Calcd for $C_8H_{18}OSi$: C, 60.69; H, 11.46. Found: C, 60.72; H, 11.47.

Cyclohexyldiphenylmethoxysilane: yield 47.5% (based on diphenyldimethoxysilane); ^1H NMR ($CDCl_3$ 250 MHz) δ 7.35–7.60 (m, 10, phenyl), 3.5 (s, 3, OCH_3), 1.45–1.57 (br s, 5, eq), 1.18–1.26 (br s, 5, ax), 0.75–0.9 (m, 1, α-Si).

Anal. Calcd for $C_{19}H_{24}OSi$: C, 77.02; H, 8.10. Found: C, 76.83; H, 7.98.

Cyclohexyldimethylmethoxysilane:[10b] yield 90% (based on dimethyldimethoxysilane); ^1H NMR ($CDCl_3$ 250 MHz) δ 3.40 (s, 3, OCH_3), 1.5–1.8 (m, 5, eq), 1.0–1.3 (m, 5, ax), 0.56–0.77 (m, 1, α-Si), −0.1 to +0.1 (s, Si-CH_3).

Irradiations of Dodecamethylcyclohexasilane and 1 in Cyclohexene and Methanol-*d*. These reactions were carried out as were the cyclopentene runs. Analysis of the 250-MHz ^1H NMR spectra showed in each case that the ratio of equatorial to axial protons was 5/4.

Registry No. 1, 18549-83-2; 3, 84960-75-8; 4, 34106-93-9; 5, 84960-76-9; 6, 54008-70-7; 7, 54960-77-0; 10, 84960-80-5; 11, 84960-79-2; 12, 54731-56-5; 13, 84960-81-6; $(Me_2Si)_6$, 4098-30-0; Me_3Si-$SiMe_3$, 1450-14-2; dichlorodimethylsilane, 75-78-5; *cis*-2-butene, 590-18-1; *trans*-2-butene, 624-64-6; *sec*-butyldimethylmethoxysilane, 73618-57-2; dichlorodiphenylsilane, 80-10-4; 2,3-dimethyl-1,3-butadiene, 513-81-5; cyclopentene, 142-29-0; diphenyl-*sec*-butylmethoxysilane, 84960-78-1; cyclohexene, 110-83-8; dimethylsilylene, 6376-86-9; diphenylsilylene, 84960-82-7.

Communications

Carbon–Hydrogen Bond Activation Using a Bis(phosphine)iridium Carbonyl Hydride and the Carbonylation of Benzene

Barbara J. Fisher and Richard Eisenberg*

Department of Chemistry, University of Rochester
Rochester, New York 14627

Received January 19, 1983

Summary: The complex $IrH_3(CO)(dppe)$ (dppe = 1,2-bis(diphenylphosphino)ethane) has been prepared from $IrI(CO)(dppe) + BH_4^-$ under H_2. Under irradiation or heating, $IrH_3(CO)(dppe)$ eliminates H_2, yielding $IrD_3(CO)(dppe)$ under D_2 and $IrH(CO)_2(dppe)$ under CO. In C_6D_6 under vacuum, $IrH_3(CO)(dppe)$ shows evidence of H/D exchange only upon irradiation, indicating arene carbon–hydrogen bond activation involving a photochemical process. When irradiation of $IrH_3(CO)(dppe)$ in C_6H_6 is performed under CO for longer times, benzaldehyde is produced as determined by NMR, GC, and organic derivatization methods. The amount of benzaldehyde formed appears to be limited thermodynamically and not kinetically. The equilibrium of the reaction $C_6H_6(l) + CO = C_6H_5CHO(l)$ is also approached by the decarbonylation of benzaldehyde. However, true equilibrium is not reached because of secondary reactions which occur upon prolonged photolysis.

Significant progress has been reported recently on the activation of carbon–hydrogen bonds by transition metal complexes. Early reports of C–H activation were based primarily on the observation of H/D exchange in hydrocarbon substrates and on the isolation of *intramolecular* C–H addition products.[1] More recent studies, however, have described the formation of stable alkyl and aryl hydride complexes via the *intermolecular* oxidative addition of C–H bonds to low-valent metal systems.[2] In this communication we describe a system which not only activates aryl C–H bonds but also inserts CO, leading to the formation of benzaldehyde. The entry point to this unusual example of C–H bond functionalization is the previously unreported Ir(III) trihydride complex $IrH_3(CO)(dppe)$, 1 (dppe = 1,2-bis(diphenylphosphino)ethane).

Complex 1 is prepared by the reaction of $NaBH_4$ and the previously unreported Ir(I) iodo complex IrI(CO)(dppe), 2, in $CH_2Cl_2/EtOH$ under H_2 as shown in eq 1.[3]

$$\underset{2}{IrI(CO)(dppe)} + BH_4^- \xrightarrow{H_2} \underset{1}{IrH_3(CO)(dppe)} \qquad (1)$$

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(1) Parshall, G. W. *Acc. Chem. Res.* **1975**, *8*, 113.

(2) (a) Janowicz, A. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1982**, *104*, 352. (b) Crabtree, R. H.; Mellea, M. F.; Mihelicic, J. M.; Quirk, J. M. *Ibid.* **1982**, *104*, 107 and references therein. (c) Hoyano, J. K.; Graham, W. A. G. *Ibid.* **1982**, *104*, 3723. (d) Barefield, E. K.; Parshall, G. W.; Tebbe, F. N. *Ibid.* **1970**, *92*, 5234. (e) Baudry, D.; Ephritikhine, M.; Felkin, H. *J. Chem. Soc., Chem. Commun.* **1980**, 1243. (f) Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1982**, *104*, 4240. (g) Hill, G. L.; Schardt, B. C. *Ibid.* **1980**, *102*, 6374. (h) Parshall, G. W. *Homogeneous Catalysis*; Wiley: New York, 1980; p 127 ff.

Table I. Spectral Data

	IR spectra		¹H NMR spectra			^{31}P NMR	
	ν_{CO}	ν_{IrH}	hydride region	methylene region	phenyl region		
$IrH_3(CO)LL$ (1)	2010	2060 2000 1940	−9.48 (d of d of d) $J_{P\text{-}H_{cis}} = -12.2$ Hz $J_{P\text{-}H_{trans}} = 124$ Hz $J_{P\text{-}H} = 4.5$ Hz −10.86 (t) $J_{P\text{-}H} = 19$ Hz	2.01 (br) 2.23 (br)	6.96 (m) 7.58 (m) 7.93 (m)	30.8 (s)	*d*
IrI(CO)LL (2)	1980			2.37 (m) 2.6 (m)	7.48 (m) 7.82 (m)	64.23 (d) 62.23 (d) $J_{P\text{-}P} = 9.1$ Hz	*e*
$IrD_3(CO)LL$ (3)	2030	*b*		same as 1	same as 1		
$IrI(CO)_2LL$ (4)	1950 2035			2.172 (d) $J_{P\text{-}H} = 18.5$ Hz	7.00 (m) 7.58 (m)	32.0 (s)	*d*
$IrH(CO)_2LL$ (5)	1912 1966	2000	−10.35 (t) $J_{P\text{-}H} = 41$ Hz	2.00 (d) $J_{P\text{-}H} = 17.1$ Hz	7.00 (m) 7.62 (m)	33.8 (s)	*d*
$IrD(CO)_2LL$ (6)	1925 1973	*b*	...	same as 5	same as 5		

[a] All IR spectra are KBr pellets recorded on a Perkin-Elmer 467 grating infrared spectrophotometer. [b] $\nu_{Ir\text{-}D}$ were not observed. [c] All ¹H NMR recorded in C_6D_6. Chemical shifts are all downfield from Me_4Si. [d] Recorded on Bruker WH-400 at 162 MHz. [e] Recorded on a Varian FT-100 spectrometer at 41.25 MHz.

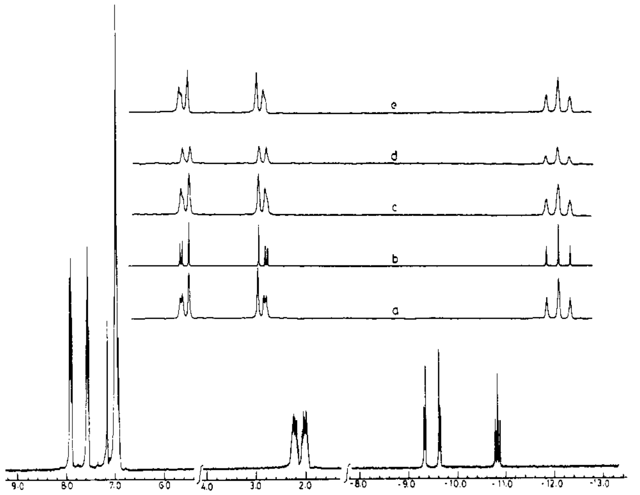

Figure 1. ¹H NMR of 1 in C_6D_6 (ppm are relative to Me_4Si): (a) expanded hydride region; (b) computer simulation of hydride region; (c) hydride region after 1 min of photolysis under D_2; (d) hydride region after 4 min of photolysis under D_2; (e) hydride region after 3 min of photolysis in C_6D_6 under vacuum. All spectra are in C_6D_6, and all expansions are from −9.1 to −11.0 ppm.

The trihydride 1 is isolated as an air-stable white powder after recrystallization. Infrared spectral data of 1 and subsequent compounds are given in Table I. On the basis of the high-resolution ¹H NMR spectrum of 1, as shown in Figure 1, a *fac* configuration for the complex can be unambiguously assigned.[5] One hydride is unique and is cis to the two dppe donor atoms, giving rise to a triplet at −10.86 ppm. The other two hydrides are chemically equivalent and are split by a trans P, a cis P, and each other (see Table I for coupling constants). The hydride–hydride coupling splits only the outermost peaks of the doublet of doublets caused by cis and trans P coupling (see Figure 1b for a computer simulation of the hydride spectrum).

Complex 1 rapidly loses H_2 both thermally and photochemically, as demonstrated by refluxing or photolyzing benzene-d_6 solutions of 1 under D_2 and CO and monitoring the ¹H NMR spectral changes with time.[6-10] In thermal or photochemical reactions under D_2, only the hydride region of the spectrum was affected. After 1 min of either photolysis or thermolysis, the outermost doublets of the −9.48 ppm resonance lose their hydride–hydride coupling (see Figure 1c) while the integrated intensities of the hydride resonances decrease significantly relative to the dppe resonances of the complex as well as to an internal integration standard. After 4 min of photolysis or thermolysis, all traces of hydride–hydride coupling are gone, and the resonance at −9.48 ppm appears as a simple doublet of doublets attributable to $IrHD_2(CO)(dppe)$ (see Figure 1d). After 8 min of either photolysis or thermolysis, less than 10% of the hydride resonances remains, indicating that

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(3) All operations were performed under N_2 by using modified Schlenk technique. (a) In a typical preparation of 1, 0.05 g of $NaBH_4$ is dissolved in 99% EtOH (10 mL) and the mixture added to a CH_2Cl_2 solution of 2 (0.1 g of 2 in 2 mL of CH_2Cl_2). The orange solution turns colorless immediately and is placed under an atmosphere of H_2 and stirred for 1 h. About 0.5 g of SiO_2 is added to solution with several drops of water. The hydrolyzed boron salts and SiO_2 are filtered from the solution, and CH_2Cl_2 is removed by rotary evaporation until the product precipitates as a tan powder, yield 0.075 g (90%). The powder can be recrystallized from hot benzene/EtOH under H_2. Anal. Calcd for $IrC_{27}H_{27}OP_2$: C, 52.2; H, 4.3; P, 9.98. Found: C, 52.4; H, 4.5; P, 9.94. (b) In a typical preparation of 2, a 0.1 g (0.25-mM) sample of dppe dissolved in 7 mL of THF is added to 0.2 g (0.26 mM) of $[Bu_4N][Ir(CO)_2I_2]$. The mixture is brought to reflux for 15 min and cooled to room temperature. Ethanol (7 mL) is added to the orange solution and the THF removed until the product precipitates as an orange powder. The product is recrystallized from hot benzene/EtOH; yield 0.1 g (50%); Anal. Calcd for $IrC_{27}H_{24}OP_2I$: C, 43.5; H, 3.2; P, 8.3. Found: C, 43.7; H, 3.5; P, 8.38.

(4) $[Bu_4N][Ir(CO)_2I_2]$ is prepared by Forster's method: Forster, D. *Inorg. Nucl. Chem. Lett.* **1969**, 5, 433.

(5) (a) All proton spectra were recorded on a Bruker WH-400 (400.134 MHz). (b) The computer simulation was determined by using the PANIC program of the ADAKOS software associated with the Bruker 400 spectrometer.

(6) (a) All thermal reactions were carried out at 85–93 °C. (b) All photolyses were carried out in sealed tubes by using a Hanovia lamp no. 679A10, unfiltered, with the sample as close to the lamp as possible.

(7) When a sample of 1 dissolved in C_6H_6 is irradiated, the evolution of bubbles can be observed. The gas evolved was shown to be H_2 by GC analysis. In addition, in sealed NMR tube experiments, a new resonance in the ¹H NMR is observed at 4.46 ppm indicative of dissolved H_2. An independent determination of the chemical shift of H_2 in C_6D_6 confirms this assignment.

(8) H_2 was detected on 12 ft of Poropak Q and 2 ft of molecular sieves (5A) at 42 °C on a Hewlett Packard 5700A gas chromatograph (TC) equipped with an HP 3380A automatic integrator.

(9) In a typical sealed tube experiment, 1.5 mg (2.4×10^{-6} M) of 1 is introduced into an NMR tube attached to a ground glass joint and the assembly is evacuated on a high vacuum line. Degassed C_6D_6 (0.8 mL) is distilled into the NMR tube, and 700 torr of the desired gas is then added. The sample is frozen in liquid N_2 and flame sealed. The concentration of 1 is ca. 3 mM compared to ca. 7 mM for CO and 3 mM for D_2 in benzene at room temperature.[10] Hexamethylethane was used as an internal integration standard.

(10) Stephen, H.; Stephen, T., Eds. "Solubilities of Inorganic and Organic Compounds"; Macmillan: New York, 1963.

deuterium incorporation is essentially complete with the conversion of 1 to 3, which based its spectral data is assigned as $IrD_3(CO)(dppe)$. When 3 dissolved in either C_6H_6 or C_6D_6 is photolyzed under H_2, it is converted back to the trihydride 1.

Thermolysis or photolysis of 1 in benzene under CO leads to the rapid appearance of a new hydride resonance at −10.35 ppm (t) accompanied by new resonances in the methylene and phenyl regions of the spectrum. After 1 min of thermolysis (93 °C in a sealed tube), 1 is 80% converted to the new compound having the triplet resonance at −10.35 ppm, while after 1 min of photolysis, ~ 50% of 1 has been converted to this product. The phenyl and methylene regions in the ^1H NMR spectrum of this new compound are nearly identical with those of the five-coordinate Ir(I) complex $IrI(CO)_2(dppe)$, 4, which forms by CO addition to 2. A larger scale photolysis of 1 under CO allows isolation of this new material which we identify as $IrH(CO)_2(dppe)$, 5, based on NMR and IR spectral data. Both 4 and 5 exhibit only sharp singlets in their $^{31}P\{^1H\}$ NMR spectra, indicating equivalence of the two dppe P donors in each complex at room temperature. Complex 5 may also be prepared from 2 and BH_4^- in dry solvents (CH_2Cl_2 + EtOH) under a CO atmosphere. The monodeuteride complex $IrD(CO)_2(dppe)$, 6, is prepared by the photolysis of 3 in C_6H_6 under CO and helps confirm the assignment of ν_{CO} and ν_{IrH} in the spectrum of 5.

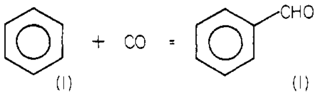
The formation of 3 and 5 by either photolysis or thermolysis of the trihydride 1 under D_2 and CO, respectively, is consistent with the notion of a reductive elimination of H_2 from $IrH_3(CO)(dppe)$, 1, generating the reactive four-coordinate species IrH(CO)(dppe), which then adds substrate molecules.

In contrast with the results for CO addition and D_2/H_2 exchange, evidence for the activation of benzene C–H bonds occurs only in photochemical experiments. When 1 is photolyzed in benzene-d_6 under vacuum, a change in the hydride spectrum is observed (see Figure 1e) which resembles that seen initially under D_2 but with C_6D_6 serving as the deuterium source. However, the exchange with benzene-d_6 is considerably slower than with D_2. After 1 min of photolysis, 90% of the intensity of the hydride resonances of 1 remains despite a *partial* loss of hydride–hydride coupling, and after 8 min of photolysis, only 50% of the hydride resonances' intensity has been lost. The fact that hydride–hydride coupling remains even after 12 min of photolysis suggests the persistence of $IrH_2D(CO)(dppe)$ in this exchange sequence in contrast with the reaction under D_2 under otherwise identical conditions.

The H/D exchange of 1 with benzene-d_6 is not observed when a solution of 1 is heated at 87 °C. No loss of hydride-hydride coupling is observed after 1.25 h of thermolysis, and the ratio of intensities of the hydride resonances to the internal standard remains constant. Further heating results in slow decomposition of the complex, but even after 5.5 h of thermolysis, the hydride resonances correspond to 55% of their initial intensity and *no* loss of hydride–hydride coupling is seen.

Further substantiation for the difference between photochemical and thermal reactivity with C–H bonds comes from experiments that lead to the carbonylation of benzene to benzaldehyde. When 1 in C_6D_6 under ~1 atm of either CO or CO/H_2 (1:1) is photolyzed for >5 h, a new resonance in the ^1H NMR spectrum at 9.63 ppm is observed which is assignable to benzaldehyde. The other observed change in the ^1H NMR spectrum is the conversion of 1 to 5 which occurs rapidly and under CO alone, completely. Experiments done to confirm the formation of benzaldehyde during the photolysis of 1 under CO and to probe its formation are summarized as follows: (1) Photolysis of 1 in C_6H_6 under 600 torr of CO followed by GC analysis of the volatiles showed benzaldehyde present.[11] Solutions which were 4–14 mM in 1 yielded solutions which were 5–8 mM in C_6H_5CHO after 8 h of photolysis.[12] (2) Photolysis of 1 under CO followed by treatment of the volatiles with semicarbazide yielded a white crystalline material which was shown to be benzaldehyde semicarbazone.[13] (3) Photolysis of 1 in C_6D_6 with a twofold excess of benzaldehyde present showed evidence for the formation of 5 within 5 min. After 8 h, the only Ir species present was 5, and the benzaldehyde resonances had decreased to a small approximately constant value with a concomitant increase in the benzene resonance.[14] (4) Thermolysis of 1 in C_6H_6 uder 600 torr of CO at 90 °C for 5 days showed *no* evidence of benzaldehyde formation by either GC or NMR methods. (5) Photolysis of 1 under conditions identical with 4 at 55 °C showed benzaldehyde formation after 6 h.

The formation of benzaldehyde when complex 1 is photolyzed in benzene under CO indicates the occurrence of eq 2. The lack of similar reaction chemistry upon thermolysis underscores the difference in photochemical and thermal reactivity of the Ir species to arene C–H bond activation. In all photolyses, the amount of benzaldehyde formed is small and appears to be limited by thermodynamics and not kinetics. We calculate $\Delta G°$ and K_{eq} at 298 °C for eq 2 as +1.7 kcal/mol and 5.9×10^{-2} atm^{-1}, respectively.[15] (Uncertainties in $S°_{298}$ for $C_6H_6(l)$ and $C_6H_5CHO(l)$ permit a range of $\Delta G°$ and K_{eq} values to be calculated, but in all cases the reaction is thermodynamically unfavorable). This notion is confirmed by 3 above, in which benzaldehyde is decarbonylated to a relatively constant value. Thus, the equilibrium of eq 2 is being approached from either direction.



(2)

Attempts to measure K_{eq} of eq 2 directly were only partially successful, yielding an average of 4.4×10^{-4} atm^{-1} at 40 °C starting with either 1 + CO + benzene or 1 + benzaldehyde in benzene under CO. However, prolonged photolysis (>36 h) shows evidence of secondary reactions. One secondary product that may prove to be highly sig-

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[11] Benzaldehyde was detected on 10 ft of Apiezon L on Chromosorb W on a Hewlett Packard 5730A GLC (FID) equipped with an HP 3380A automatic integrator. GLC conditions: oven, 150 °C; detector, 200 °C; injector, port, 250 °C.

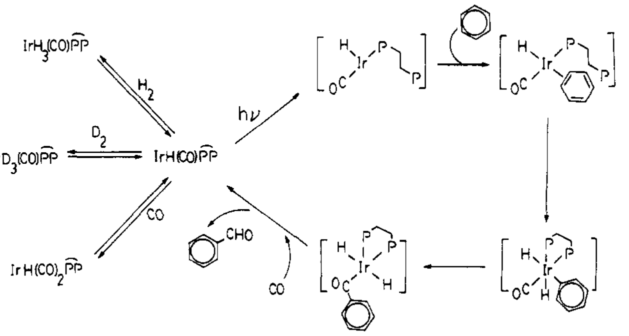
[12] In these photolyses, the light from the lamp was not attenuated or quantitatively filtered. Therefore exact yield of photolysis products cannot be measured at accurate time intervals. The results reported here represent the real spread due to different light intensities.

[13] Shriner, R. L.; Fuson, R. C.; Curtin, D. Y. "The Systematic Identification of Organic Compounds"; Wiley: New York, 1959. In our derivatization, the distilled benzene solution obtained from the photolysis was used without an attempt to separate the benzaldehyde from it. After the condensation was complete, the benzene was removed, and the semicarbazone precipitated immediately. The samples obtained in this way were compared with a sample of benzaldehyde semicarbazone prepared using authentic benzaldehyde and the slightly modified procedure described above.

[14] Photolysis of 1 with much a larger fold excess of benzaldehyde shows evidence of secondary reactions. Thermolysis of 1 with benzaldehyde present also leads to benzaldehyde decarbonylation.

[15] This range of values may be calculated with thermodynamic constants from the following sources: Wenner, R. R. "Thermochemical Calculations"; McGraw Hill: New York, 1941. Benson, S. W. "Thermochemical Kinetics"; Wiley-Interscience: New York, 1976. "Handbook of Chemistry and Physics", 62nd ed.; CRC Press: Boca Raton, 1981. Entropy values of benzene and benzaldehyde are adjusted for the liquid phase.

Scheme I



nificant is benzyl alcohol,[16] since the reduction of benzaldehyde to benzyl alcohol is thermodynamically favorable. This reaction may thus serve as a drain for the carbonylation of benzene to benzaldehyde and efforts in this direction are in progress.

The mechanism by which benzene C–H activation occurs is clearly photochemical and is not simply analogous to H_2 oxidative addition. One possibility is that the intermediate species IrH(CO)(dppe), which forms readily under either photolysis or thermolysis conditions, undergoes a photochemical dissociation of a ligand to form a 14-electron species facilitating arene coordination prior to oxidative addition. Alternatively, we may be witnessing an example of a photochemical oxidative addition reaction. Once the benzene C–H bond is activated, the carbonylation reaction probably follows the expected path of insertion and reductive elimination. We summarize the observed reaction chemistry and these mechanistic proposals in Scheme I.

Acknowledgment. We wish to thank the National Science Foundation (Grant CHE80-11974) and the Office of Naval Research for support of this work, as well as the Sherman Clarke Foundation for a fellowship to B.J.F. We also thank the Johnson Matthey Co., for a generous loan of precious metal salts and acknowledge Professor William Jones, Professor Jack Kampmeier, Dr. Curt Johnson, and Mr. Frank Feher for helpful discussions.

Registry No. 1, 85421-67-6; 2, 85421-68-7; 3, 85421-69-8; 4, 85421-70-1; 5, 85421-71-2; 6, 85421-72-3; dppe, 1663-45-2; $[Bu_4N][Ir(CO)_2I_2]$, 60255-19-8; C_6H_6, 71-43-2; benzaldehyde, 100-52-7.

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[16] Benzyl alcohol was detected and quantified by GLC (FID) on a combination column consisting of 10 ft of Apiezon L on Chromosorb W and 10 ft of 20% SE-30 on Chromosorb W using the same GLC conditions as in ref 11. Its formation was confirmed by coinjection with an authentic sample of $C_6H_5CH_2OH$ on this column, by ^1H NMR and mass spectral analysis.

Photochemistry of Dipalladium(I) Hexakis(methyl isocyanide) Hexafluorophosphate

Terry D. Miller, Martin A. St. Clair, Mark K. Reinking, and Clifford P. Kubiak*

Department of Chemistry, Purdue University
West Lafayette, Indiana 47907

Received December 7, 1982

Summary: The photochemistry of $[Pd_2{}^I(CNCH_3)_6]\cdot 2(PF_6)$ in the presence of halogen atom donors CX_4 (X = Cl, Br) is found to lead to halogen atom abstraction yielding $[Pd^{II}X(CNCH_3)_3]$ PF_6. Cross coupling of $\cdot Pd^I(CNCH_3)_3{}^+$ and $\cdot Pt^I(CNCH_3)_3{}^+$ radical fragments gives heteronuclear $[PdPt(CNCH_3)_6]\cdot 2(PF_6)$ when the homonuclear species $[Pd_2{}^I(CNCH_3)_6]\cdot 2(PF_6)$ and $[Pt_2{}^I(CNCH_3)_6]\cdot 2(PF_6)$ are irradiated together. Homonuclear species are obtained when $[PdPt(CNCH_3)_6]\cdot 2(PF_6)$ is irradiated. These results are interpreted in terms of the photogeneration of reactive 15 valence electron species $\cdot Pd^I(CNCH_3)_3{}^+$ via homolysis of the Pd–Pd bond in $\sigma_b \rightarrow \sigma^*$ or $d\pi \rightarrow \sigma^*$ excited states. Quantum yields for the disappearance of $[Pd_2{}^I(CNCH_3)_6]\cdot 2(PF_6)$ in the presence of CX_4 (X = Cl, Br) are high, $\Phi_{dis_{313}} = 0.42$ (CCl_4) and 0.70 (CBr_4), suggesting efficient cleavage of a Pd–Pd bond in the excited state. UV photolysis of $[Pd_2{}^I(CNCH_3)_6]\cdot 2(PF_6)$ in CH_3CN frozen solution at 150 K in an EPR cavity leads to the observation of a metal based radical with $g \simeq 2.12$.

We wish to report the first observation of photochemistry of a Pd–Pd metal–metal bond. The photochemistry of metal–metal bonds has been an area of intense interest.[1-34] Complexes having metal–metal single bonds, no-

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