Photochemical Intermolecular Oxidative Addition of the C−Cl Bond of Chlorobenzene to Rhenium

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The phenyl chloride complexes Cp*Re(CO)(L)(Ph)Cl (L = $P(OEt)_3$ (**6**), Pc (**7**), $P(OMe)_3$ (**8**), and PMe_2Ph (**9**)) have been prepared by irradiation of the corresponding rhenium dinitrogen complex Cp*Re(CO)(L)(N_2) in chlorobenzene. In the case of L = $P(OPh)_3$ the result was instead the formation of the cyclometalated complex Cp*Re(CO){η^2-$P(OC_6H_4)(OPh)_2$}H (**10**), arising from intramolecular C−H oxidative addition of a phenyl group of the phosphine oxide ligand.

Introduction

Numerous examples of the oxidative addition of *alkyl* halides to coordinatively unsaturated transition metal complexes are known, particularly involving d^{10} Ni(0), Pd(0), and Pt(0) and d^8 Co(I), Rh(I), and Ir(I) complexes.[1] In the case of *aryl* halides, there are fewer examples, and these mainly have involved the bromides and iodides.[1,2] Catalytic activation of the carbon−halogen bond of haloarenes is of considerable importance in olefination and carbonylation reactions such as the Heck reaction.[3] Despite this, the oxidative addition of the C−Cl bond in aryl chlorides to form characterizable products has been limited to relatively few examples, and this lack of reactivity reflects the relative strength of this bond (ca. 96 kcal mol^{-1} in chlorobenzene) compared with C−Br or C−I, although mechanistic factors must be considered.[3a] Chlorobenzene has been shown to react with $Ni(PPh_3)_3$, Ni(bipy)Et_2, $Ni(PEt_3)_4$, Ni(COD)L_2 (L = bipy or tmed), $Pd(PPh_3)_4$, $Pd(PPh_3)_2$(dba), Pd(P(cyclohexyl)$_3$)$_2$(dba), Pd(dippp)$_2$, $Pd(PEt_3)_3$, $Pt(PEt_3)_3$, and Pt{P(cyclohexyl)$_3$}$_2$.[4−10] It was reported to react with Vaska's compound *trans*-IrCl(CO)$(PPh_3)_2$ to give evidence of the oxidative addition product (ν_{CO} = 2050 cm^{-1}), but this could not be isolated pure.[11] Electrochemically reduced cobalt complexes also react,[12] as do some uranium complexes.[13] When activated by complexation through its π system to iron, it has also been shown to oxidatively add to $Pd(PPh_3)_4$.[14] A further strategy for activation has been the incorporation of the aryl C−Cl bond in a metal-bound ligand, which facilitates *intra*molecular oxidative addition.[15] Gladysz has documented the *ligation* of chlorobenzene to rhenium at low temperature in complexes of the type [Cp*Re(NO)(PPh_3)(ClC_6H_5)][BF_4]. While these undergo spectroscopic changes on warming, and the formation of a C−Cl oxidative addition product may result, this could not be conclusively identified.[16]

In this paper, we report the oxidative addition of chlorobenzene to half-sandwich rhenium phosphine and phosphite complexes under photochemical conditions. We can find few references to previous photochemical reactions of transition metal complexes and chlorobenzene.[17] The photochemical carbonylation of haloarenes in the presence of catalytic amounts of $Co_2(CO)_8$ has been reported, but here chlorobenzene was unreactive.[18a]

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[1] For accounts of oxidative addition see for example: (a) Collman, J. P.; Roper, W. R. *Adv. Organomet. Chem.* **1968**, *7*, 53. (b) Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*, 2nd ed.; Wiley: New York, 1994; Chapter 6, p 121. (c) Lukehart, C. M. *Fundamental Transition Metal Organometallic Chemistry*; Brooks/Cole Publishing Company: Monterey, CA, 1985; Chapter 10, p 274. (d) Mondal, J. U.; Blake, D. M. *Coord. Chem. Rev.* **1982**, *47*, 205. (e) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; Chapter 5. (f) Stille, J. K. In *The Chemistry of the Metal−Carbon Bond*; Hartley, F. R., Patai, S., Eds; Wiley: New York, 1985; Vol. 2, Chapter 9. (g) Kochi, J. K. *Organometallic Mechanisms and Catalysis*; Academic Press: New York, 1978; Part I, Chapter 7, pp 156−183.

[2] Kochi, J. K. *Organometallic Mechanisms and Catalysis*; Academic Press: New York, 1978; Part I, Chapter 7, p 168.

[3] (a) For a recent review on the activation of chloroarenes by transition metals, see: Grushin, V. V.; Alper, H. *Chem. Rev.* **1994**, *94*, 1047. (b) Grushin, V. V.; Alper, H. *Organometallics* **1993**, *12*, 1890. (c) Hidai, M.; Kashiwagi, T.; Ikeuchi, T.; Uchida, Y. *J. Organomet. Chem.* **1971**, *30*, 279. (d) Foa, M.; Cassar, L. *J. Chem. Soc., Dalton Trans.* **1975**, 2572. (e) Uchino, M.; Yamamoto, A.; Ikeda, S. *J. Organomet. Chem.* **1970**, *24*, C63.

[4] (a) Kochi, J. K. *Pure. Appl. Chem.* **1980**, *52*, 571. (b) Wenschuh, E.; Zimmering, R. *Z. Chem.* **1987**, *27*, 448. (c) Fahey, D. R.; Mahan, J. E. *J. Am. Chem. Soc.* **1977**, *99*, 2501. (d) Tsou, T. T.; Kochi, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 6319.

[5] Herrmann, W. A.; Brossmer, C.; Priermeier, T.; Ofele, K. *J. Organomet. Chem.* **1994**, *481*, 97.

[6] Portnoy, M.; Milstein, D. *Organometallics* **1993**, *12*, 1665.

[7] (a) Huser, M.; Youinou, M.-T.; Osborn, J. A. *Angew. Chem., Int. Ed. Engl.* **1989**, *38*, 1386. (b) Coulson, D. R. *J. Chem. Soc., Chem. Commun.* **1968**, 1530.

[8] Gerlach, D. H.; Kane, A. R.; Parshall, G. W.; Jesson, J. P.; Muetterties, E. L. *J. Am. Chem. Soc.* **1971**, *93*, 3543.

[9] Fornies, J.; Green, M.; Spencer, J. L.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1977**, 1006.

[10] Rieke, R. D.; Kavaliunas, A. V. *J. Org. Chem.* **1979**, *44*, 3069.

[11] Blum, J.; Weitzberg, M.; Mureinik, R. J. *J. Organomet. Chem.* **1976**, *122*, 261.

[12] (a) Pilloni, G.; Valcher, S.; Martelli, M. *J. Electroanal. Chem.* **1972**, *40*, 63. (b) Zecchin, S.; Schiavon, G.; Pilloni, G.; Martelli, M. *J. Organomet. Chem.* **1976**, *110*, C45.

[13] Finke, R. G.; Hirose, Y.; Gaughan, G. *J. Chem. Soc., Chem. Commun.* **1981**, 232.

[14] Aoki, T.; Ishii, Y.; Mizobe, Y.; Hidai, M. *Chem. Lett.* **1991**, 615.

[15] See, for example: (a) Anderson, C. M.; Crespo, M.; Jennings, M. C.; Lough, A. J.; Ferguson, G.; Puddephatt, R. *Organometallics* **1991**, *10*, 2672, and references therein. (b) Kiplinger, J. L.; Richmond, T. G. *Polyhedron* **1997**, *16*, 409.

[16] (a) Peng, T.-S.; Winter, G. H.; Gladysz, J. A. *Inorg. Chem.* **1994**, *33*, 2534. (b) Kowalczyk, J. J.; Agbossou, S. K.; Gladysz, J. A. *J. Organomet. Chem.* **1990**, *397*, 333.

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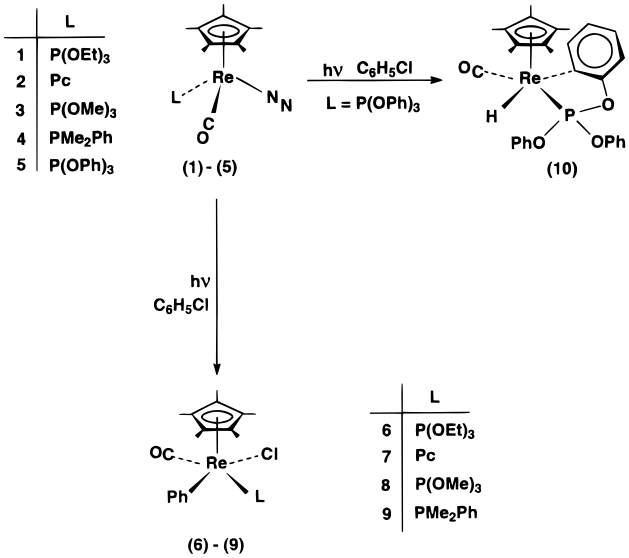
Scheme 1. Photolysis of the Dinitrogen Complexes 1−5 in Chlorobenzene (Pc = P(OCH$_2$)$_3$CMe)



However, Trogler and co-workers have shown that Pt(PEt$_3$)$_2$ generated by irradiation of the oxalate complex Pt(C$_2$O$_4$)(PEt$_3$)$_2$ reacts immediately with chlorobenzene to give *trans*-Pt(PEt$_3$)$_2$(Ph)Cl.[18b] This may be compared with the longer times required for corresponding thermal reactions.[8,9] Apart from our continuing interest in the photochemistry of rhenium dinitrogen complexes in promoting C−H bond activation,[19−23] we were prompted to attempt the synthesis of authentic rhenium phenyl chloride complexes in this way in view of the fact that we had previously observed that related unstable photogenerated phenyl hydride complexes, e.g., Cp*Re(CO)(Pc)(Ph)H (Pc = P(OCH$_2$)$_3$CMe) did not appear to form the corresponding phenyl chloride complex when treated with a chlorinated solvent.[19]

Results

The complexes of general formula Cp*Re(CO)(L)(Ph)Cl (L = P(OEt)$_3$ (**6**), Pc (**7**), P(OMe)$_3$ (**8**), and PMe$_2$Ph (**9**)) were prepared by irradiation of the corresponding rhenium dinitrogen complex (**1**−**4**) in chlorobenzene (Scheme 1). These complexes were purified by chromatographic techniques and were obtained as yellow-orange microcrystalline solids in greater than 60% yield by recrystallization from hexane−benzene. They are air-stable in the solid state and in solution. The complexes **6**−**9** were obtained only as the isomer in which the phenyl group is trans to chloride. These new complexes have been identified by IR, ^{1}H NMR, ^{13}C{^{1}H} NMR, and mass spectroscopies.

Contrasting with the above, irradiation of the triphenyl phosphite dinitrogen complex Cp*Re(CO){P(OPh)$_3$}(N$_2$) (**5**) under similar conditions gave the orthometalated C−H activation product Cp*Re(CO){η^2-P(OC$_6$H$_4$)(OPh)$_2$}H (***cis(P−H)*-10**), which was characterized by ^{1}H NMR and mass spectroscopies and shown to be identical to the complex obtained previously from the photolysis of Cp*Re(CO){P(OPh)$_3$}(N$_2$) in hydrocarbons.[19]

The IR spectra of **6**−**9** exhibited a single ν_{CO} absorption in the range 1867−1898 cm^{-1}. The ^{1}H NMR spectrum of **6** exhibited the expected resonances for Cp*, phosphite, and phenyl ligands. The aromatic region for **6** clearly showed the presence of three distinguishable proton environments corresponding to the ortho-, meta-, and para-position protons of the phenyl ligand: a multiplet at δ 6.94 (relative integral area 1H) assigned to the *p*-proton, a multiplet at δ 7.09 (relative integral 2H) assigned to the *m*-protons, and a high field multiplet at δ 7.92 (relative integral 2H) assigned to the *o*-protons. These assignments are similar to those established previously for CpRe(CO)(NO)Ph and related substituted phenyl complexes by using NOE and decoupling experiments.[24] Corresponding ^{1}H NMR spectra were observed for the complexes **7**−**9,** but for **9** the phenyl resonances from the phenyl ligand and the PMe$_2$Ph ligand were overlapped.

In the ^{13}C{^{1}H} NMR spectra of complexes **6**, **7**, and **9** the aromatic carbons showed their expected resonances in the region δ 120−145, and the carbonyl resonance generally was split into a doublet with $^2J_{C-P}$ values of 15−34 Hz. (The Pc complex **7** exhibited the carbonyl resonance only as a singlet, and we presume that $^2J_{C-P}$ was too small to be observed.) The magnitude of these coupling constants suggests that the phosphorus group in these four-legged “piano stool” complexes is trans to the carbonyl moiety.[25] An appreciable downfield shift for the carbonyl carbon resonance was observed in the ^{13}C{^{1}H} NMR spectra in Cp*Re(CO)(L)(Ph)Cl as L is changed in the sequence L = Pc, P(OMe)$_3$, P(OEt)$_3$, and PMe$_2$Ph. The overall magnitude of the shift was ~30 ppm. A similar observation has been reported in R$_3$PNi(CO)$_3$ (R = alkyl or alkoxy) complexes.[26]

The EI mass spectrum of **6** gave a weak parent M$^+$ peak at *m*/*z* 628, the base peak at *m*/*z* 600 corresponded to the loss of CO, and then loss of C$_6$H$_6$ gave a fragment of *m*/*z* 522. The complexes **7** and **8** showed corresponding fragmentation patterns. The EIMS spectrum of **7** did not give a parent M$^+$ peak, but a base peak was observed at *m*/*z* 523, corresponding to the loss of C$_6$H$_5$.

The IR spectrum for ***cis(P−H)*-10** showed a single ν_{CO} absorption at 1927 cm^{-1} in CH$_2$Cl$_2$. In the ^{1}H NMR spectrum obtained in CDCl$_3$, a set of multiplets in the range δ 6.80−7.41 in the aromatic region with total relative integral 14H were assigned to the orthometalated phenyl phosphite moiety. The spectrum also

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[17] In unpublished work, Klahn and co-workers have studied the photolysis of CpRe(CO)$_3$ and Cp*Re(CO)$_3$ with pentachlorobenzene, resulting in C−Cl oxidative addition. Klahn, A. H. Personal communication.

[18] (a) Brunet, J.-J.; Sidot, C.; Caubere, P. *J. Org. Chem.* **1983**, *48*, 1166. (b) Paonessa, R. S.; Prigano, A. L.; Trogler, W. C. *Organometallics* **1985**, *4*, 647.

[19] Leiva, C.; Sutton, D. *Organometallics* **1998**, *17*, 1700.

[20] Aramini, J. M.; Einstein, F. W. B.; Jones, R. H.; Klahn-Oliva, A. H.; Sutton, D. *J Organomet. Chem.* **1990**, *385*, 73.

[21] Zhuang, J.-M.; Sutton, D. *Organometallics* **1991**, *10*, 1516.

[22] Batchelor, R. J.; Einstein, F. W. B.; Jones, R. H.; Zhuang, J.-M.; Sutton, D. *J. Am. Chem. Soc.* **1989**, *111*, 3468.

[23] Klahn Oliva, A. H.; Singer, R. D.; Sutton, D. *J. Am. Chem. Soc.* **1986**, *108*, 3107.

[24] (a) Sweet, J. R.; Graham, W. A. G. *Organometallics* **1983**, *2*, 135. (b) Hunter, B. K.; Baird, M. C. *Organometallics* **1985**, *4*, 1481.

[25] (a) Gibson, D. H.; Franco, J. O.; Richardson, J. F. *Organometallics* **1993**, *12*, 860. (b) Todd, L. J.; Wilkinson, J. R.; Hickey, J. P.; Beach, D. L.; Barnett, K. W. *J Organomet. Chem.* **1978**, *154*, 151.

[26] Bodner, G. M.; May, M. O.; McKinney, L. E. *Inorg. Chem.* **1980**, *19*, 1951.

exhibited a doublet in the metal hydride region at δ -10.12, with a relative integral 1H, and $J_{P-H} = 61.0$ Hz. The ^{1}H NMR and mass spectroscopic data for this product were compared with the same product obtained in the reaction of **5** with hydrocarbons and are in agreement.[19]

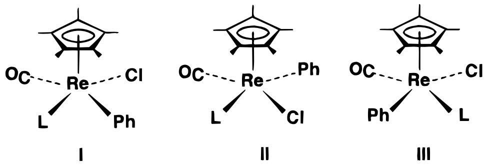
When Cp*Re(CO){P(OEt)$_3$}(Ph)Cl (**6**) or Cp*Re(CO)(PMe$_2$Ph)(Ph)Cl (**9**) was stirred in either CHCl$_3$ or CCl$_4$ at room temperature for 6 h or under reflux for 5 h, no change of ν_{CO} was observed in the IR spectrum. When Cp*Re(CO){η^2-P(OC$_6$H$_4$)(OC$_6$H$_5$)$_2$}H (***cis(P−H)*-10**) was dissolved in CHCl$_3$ and stirred under nitrogen overnight at room temperature, the ^{1}H NMR and IR spectra of recovered material in CDCl$_3$ and CHCl$_3$, respectively, showed no evidence of deterioration or exchange of the hydride ligand with chlorine. A solution of ***cis(P−H)*-10** in chlorobenzene at 313 K for 2 h under nitrogen, or heated under refluxing conditions for 3 h, showed no evidence of change by IR spectroscopy.

Discussion

In previous work, we had observed the formation, in solution, of the phenyl hydride complexes Cp*Re(CO)(L)(Ph)H (L = P(OEt)$_3$ or Pc) when the dinitrogen complexes **1** and **2** were irradiated in benzene.[19] In an effort to convert these to more stable phenyl chloride complexes, so as to permit isolation and identification, the solutions were treated with either CHCl$_3$ or CCl$_4$. Unstable alkyl or aryl hydride complexes have been known to be stabilized in the halide form by treatment with a halogenated solvent to generate the more stable alkyl or aryl halide complex.[27] However, we found this did not afford the corresponding phenyl chloride complex. Instead, the only species detectable was the rhenium dichloride complex Cp*Re(CO)(L)Cl$_2$.[19] Consequently, we were interested in attempting to prepare the expected phenyl chloride complexes Cp*Re(CO)(L)(Ph)Cl by an alternative method in order to assess their stabilities. It was possible that these species were, in fact, the primary products of reaction of the unstable phenyl hydride complex Cp*Re(CO)(L)(Ph)H with the halogenated solvent, but that they reacted further to give the dichloride complexes. Therefore, in an attempt to prepare Cp*Re(CO)(L)(Ph)Cl, we investigated the photolysis of the rhenium dinitrogen complexes Cp*Re(CO)(L)(N$_2$) (L = P(OMe)$_3$, P(OEt)$_3$, P(OPh)$_3$, PMe$_2$Ph, and Pc) (**1**−**5**) (Scheme 1) in chlorobenzene and the reactivity toward chlorinated solvents of the product formed.

When the complexes Cp*Re(CO)(L)(N$_2$) (L = P(OEt)$_3$, Pc, P(OMe)$_3$, PMe$_2$Ph, and P(OPh)$_3$) are irradiated in chlorobenzene, intermediates of the type [Cp*Re(CO)(L)] are proposed to be generated by loss of N$_2$, as in the case of photolysis in hydrocarbons.[20,23,28] These reactive 16-electron intermediates are then considered to undergo oxidative addition of the C−Cl bond of chlorobenzene to give the observed phenyl chloride complexes. In the case of oxidative addition of C$_6$F$_6$ to rhodium, it was established that a C$_6$F$_6$ π-complex is formed first and undergoes further photolysis to give the rhodium pentafluorophenyl fluoride oxidative addition product.[29] A corresponding chlorobenzene π-complex is a plausible intermediate in the present case. None was detected, however, so it was not possible to determine whether the C−Cl oxidative addition step is photochemical or thermal.

Chart 1. Possible Isomers for the Phenyl Chloride Complexes 6−9 (L = Phosphite or Phosphine Ligand)



Three isomers are theoretically possible for the four-legged piano-stool configuration of the product (Chart 1). Isomer **III** is the only one in which the CO and P are mutually trans. The stereochemistry depicted in **III** was deduced on the basis of the observed $^2J_{C-P}$ value for δ_{CO} in the ^{13}C{^{1}H} NMR spectra. Typical $^2J_{C-P}$ values for this situation are in the range 0−15 Hz. In isomer **I** and **II** the CO and P are mutually cis. In this situation the $^2J_{C-P}$ value is generally expected to be greater than 30 Hz.[25] The formation of the isomer in which the added fragments are mutually trans may be compared with earlier results on the photolysis of the trimethylphosphine complexes Cp*Re(CO)$_2$(PMe$_3$) or Cp*Re(CO)(PMe$_3$)(N$_2$) in benzene, where the observed phenyl hydride complex is similar.[20,23,28]

The values for ν_{CO} in the phenyl chloride complexes followed the order Pc > P(OMe)$_3$ > P(OEt)$_3$ > PMe$_2$Ph, which correlates with the expected σ-donor and π-acceptor ability of the phosphorus ligand. This effect was reiterated in the ^{13}C chemical shift of the carbonyl group, where the complex with the better σ-donor/poorer π-acceptor showed a more upfield resonance.[26]

The photolysis of Cp*Re(CO){P(OPh)$_3$}(N$_2$) (**5**) in chlorobenzene did not give a corresponding phenyl chloride complex, but gave instead only Cp*Re(CO){η^2-P(OC$_6$H$_4$)(OC$_6$H$_5$)$_2$}H (**10**), the product of intramolecular C−H activation, and no evidence of oxidative addition of the C−Cl bond of chlorobenzene was observed. Therefore, in this reaction intramolecular activation of an ortho C−H bond of the triphenyl phosphite ligand competed effectively with intermolecular C−Cl bond activation of chlorobenzene. Likewise, Cp*Re(CO){P(OPh)$_3$}(N$_2$) (**5**) did not undergo intermolecular C−H activation of benzene to produce the phenyl hydride complex when irradiated in this solvent.[19] These results clearly suggest that for the triphenyl phosphite ligand ortho-metalation is kinetically (and perhaps thermodynamically) favored over intermolecular C−H or C−Cl oxidative addition. The treatment of Cp*Re(CO){η^2-P(OC$_6$H$_4$)(OC$_6$H$_5$)$_2$}H (***cis(P−H)*-10**) with CHCl$_3$ or PhCl under forcing conditions did not replace the hydride with a chloride ligand nor form a phenyl chloride complex.

Also, no reaction occurred when Cp*Re(CO){P(OEt)$_3$}(Ph)Cl (**6**) and Cp*Re(CO)(PMe$_2$Ph)(Ph)Cl (**9**) were

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[27] (a) Janowicz, A. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1982**, *104*, 352. (b) Janowicz, A. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 3929.

[28] (a) Bergman, R. G.; Seidler, P. F.; Wenzel, T. T. *J. Am. Chem. Soc.* **1985**, *107*, 4358. (b) Wenzel, T. T.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 4856.

[29] Belt, S. T.; Helliwell, M.; Jones, W. D.; Partridge, M. G.; Perutz, R. N. *J. Am. Chem. Soc.* **1993**, *115*, 1429.

treated with chlorinated solvents. This result means that the complexes Cp*Re(CO)(L)(Ph)Cl were not intermediates in the production of the rhenium dichloride complexes $Cp^*Re(CO)(L)Cl_2$ observed in the reaction of Cp*Re(CO)(L)(Ph)H with chlorinated solvents.[19] To account for this, it is possible that the phenyl hydride complexes undergo reductive elimination of benzene to give the 16-electron intermediates [Cp*Re(CO)L], which then react with the chlorinated solvent.

Conclusion

In this paper we have demonstrated that rhenium phosphite and phosphine dinitrogen complexes $Cp^*Re(CO)(L)(N_2)$, where L = $P(OEt)_3$, Pc, $P(OMe)_3$, and PMe_2Ph, react with chlorobenzene under photochemical conditions to produce stable rhenium phenyl chloride complexes. As far as we know, this is the first demonstration of oxidative addition of an aryl chloride in a rhenium system to give well-characterized products.[17] The only isomer isolated under these conditions was the presumably more thermodynamically stable trans isomer. However, under similar conditions, the triphenyl phosphite complex $Cp^*Re(CO)\{P(OPh)_3\}(N_2)$ gave the product of intramolecular C−H activation rather than intermolecular C−Cl bond activation.

Experimental Section

General Methods. All manipulations were performed under nitrogen by using standard Schlenk or vacuum line techniques unless stated otherwise. Photolyses were carried out at atmospheric pressure and at 277 K with a water-jacketed 200 W Hanovia medium-pressure mercury arc lamp as the UV source. The reactions were conducted under a nitrogen flow in a Pyrex tube which was placed adjacent to the lamp. Chlorobenzene was distilled over $CaSO_4$ and transferred directly into the Pyrex reaction tube under nitrogen. Hexane, benzene, and dichloromethane were dried using standard methods and distilled under nitrogen.

All the NMR data were recorded on a Bruker AMX 400 instrument at an operating frecuency of 400 and 100 MHz for ^1H and ^{13}C nuclei, respectively. The ^1H and $^{13}C\{^1H\}$ NMR chemical shifts are reported in ppm downfield (positive) of tetramethylsilane. The deuterated solvents used for NMR spectroscopy were degassed prior to use.

Infrared spectra were measured by using a Bomem Michelson model 120 FT-IR instrument, usually as solutions in CaF_2 cells. Mass spectra were obtained with a Hewlett-Packard model 5985 mass spectrometer. Masses are quoted for the ^{35}Cl and ^{187}Re isotopes. Microanalyses were performed by Simon Fraser University Microanalytical Laboratory.

Syntheses. Details of the preparation and characterization of $Cp^*Re(CO)(L)(N_2)$ (L = $P(OEt)_3$ (**1**), Pc (**2**), $P(OMe)_3$ (**3**), and $P(OPh)_3$ (**5**)) have been given in previously.[19,30] $Cp^*Re(CO)(PMe_2Ph)(N_2)$ (**4**) was synthesized similarly. Data for **4**: IR (hexane): ν_{N2} 2010, ν_{CO} 1863 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.79 (s, 15H, C_5Me_5), 1.85 (d, 3H, PMe_2Ph, $J_{P-H} = 9.0$ Hz), 1.87 (d, 3H, PMe_2Ph, $J_{P-H} = 9.0$ Hz), 7.30−7.55 (m, 5H, PMe_2Ph). $^{31}P\{^1H\}$ NMR (benzene-d_6): δ 16.28. MS (EI): m/z 516 (M^+), 488 ($M^+ - N_2$), 460 ($M^+ - N_2 - CO$). Anal. Calcd for $C_{19}H_{26}N_2OPRe$: C, 44.26; H, 5.08; N, 5.43. Found: C, 44.23; H, 5.04; N, 5.36.

Photolysis of $Cp^*Re(CO)\{P(OEt)_3\}(N_2)$ (1) in Chlorobenzene. A solution of the triethyl phosphite dinitrogen complex **1** (30 mg, 0.055 mmol) in chlorobenzene (10 mL) was irradiated in a Pyrex tube for 12 min. An IR spectrum of the resulting orange-red solution showed the total disappearance of the dinitrogen complex. The solvent was removed under vacuum at room temperature, and the residue was redissolved in ca. 2 mL of benzene and transferred to an air-free neutral alumina column prepared in hexane and eluted with benzene−hexane (3:1). Removal of the solvent under vacuum gave a yellow-orange solid, which was recrystallized from a benzene−hexane mixture at 269 K to provide **6** as a yellow solid in 70% yield (25 mg, 0.039 mmol). IR (CH_2Cl_2): ν_{CO} 1884 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.26 (t, 9H, $P(OCH_2CH_3)_3$, $J_{H-H} = 7.0$ Hz), 1.61 (s, 15H, C_5Me_5), 4.12 (m, 6H, $P(OCH_2CH_3)_3$), 6.94 (m, 1H, p-C_6H_5, $J_{H-H} = 7.7$ Hz), 7.09 (m, 2H, m-C_6H_5, $J_{H-H} = 7.4$ Hz), 7.92 (m, 2H, o-C_6H_5, $J_{H-H} = 8.2$ Hz, $J_{H-H} = 1.0$ Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 9.95 (s, C_5Me_5), 16.14 (d, $P(OCH_2CH_3)_3$, $J_{C-P} = 5.7$ Hz), 64.56 (d, $P(OCH_2CH_3)_3$, $J_{C-P} = 8.3$ Hz), 101.57 (s, C_5Me_5), 123.41 (s, p-C_6H_5), 126.94 (s, m-C_6H_5), 141.70 (s, o-C_6H_5), 207.10 (d, CO, $J_{C-P} = 20.0$ Hz). MS (EI): m/z 628 (M^+), 600 ($M^+ - CO$), 522 ($M^+ - CO - C_6H_6$). Anal. Calcd for $C_{24}H_{35}O_4ClPRe$: C, 45.03; H, 5.51. Found: C, 45.08; H, 5.56.

Photolysis of $Cp^*Re(CO)(Pc)(N_2)$ (2) in Chlorobenzene. A solution of the Pc dinitrogen complex **2** (15 mg, 0.030 mmol) in chlorobenzene (6 mL) was irradiated in a Pyrex tube for 12 min. An IR spectrum of the resulting yellow-red solution showed the total disappearance of the dinitrogen complex. The solvent was removed under vacuum, and the residue was washed with two portions (2 mL) of hexane, redissolved in benzene, and filtered through a short neutral alumina column. The fraction containing the product was evaporated and the residue was recrystallized from benzene−hexane at 269 K to afford **7** in 61% yield (12 mg, 0.018 mmol). IR (CH_2Cl_2): ν_{CO} 1898 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.81 (s, 3H, $P(OCH_2)_3CCH_3$), 1.69 (s, 15H, C_5Me_5), 4.33 (d, 6H, $P(OCH_2)_3CCH_3$, $J_{H-P} = 5.4$ Hz), 6.93 (m, 1H, p-C_6H_5, $J_{H-H} = 7.1$ Hz), 7.06 (m, 2H, m-C_6H_5, $J_{H-H} = 7.7$ Hz), 7.81 (m, 2H, o-C_6H_5, $J_{H-H} = 7.6$ Hz, $J_{H-H} = 1.0$ Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 10.09 (s, C_5Me_5), 15.54 (s, $P(OCH_2)_3CCH_3$), 32.94 (d, $P(OCH_2)_3CCH_3$, $J_{C-P} = 33.5$ Hz), 76.84 (d, $P(OCH_2)_3CCH_3$, $J_{C-P} = 8.0$ Hz), 102.16 (s, C_6H_5), 123.52 (s, C_6H_5), 127.32 (d, C_6H_5), 141.87 (s, C_6H_5), 194.29 (s, CO). MS (EI, 12 eV): m/z 610 (M^+) 582 ($M^+ - CO$). Anal. Calcd for $C_{22}H_{29}O_4ClPRe$: C, 43.31; H, 4.79. Found: C, 43.58; H, 4.88.

Photolysis of $Cp^*Re(CO)\{P(OMe)_3\}(N_2)$ (3) in Chlorobenzene. A solution of the trimethyl phosphite dinitrogen complex **3** (30 mg, 0.060 mmol) in chlorobenzene (5 mL) was irradiated in a Pyrex tube for 6 min. An IR spectrum of the resulting yellow-orange solution showed the total disappearance of the dinitrogen complex. After the irradiation, the solvent was removed under vacuum at room temperature and the residue was extracted with benzene. The product was chromatographed on a neutral alumina column made up in hexane and eluted with benzene−hexane (5:1). Recrystallization from benzene−hexane at 269 K gave **8** in 60% yield (21 mg, 0.036 mmol). IR (CH_2Cl_2): ν_{CO} 1889 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.62 (s, 15H, C_5Me_5), 3.76 (d, 9H, $P(OMe)_3$, $J_{H-P} = 8.9$ Hz), 6.95 (m, 1H, p-C_6H_5, $J_{H-H} = 7.5$ Hz), 7.09 (m, 2H, m-C_6H_5, $J_{H-H} = 7.5$ Hz), 7.92 (m, 2H, o-C_6H_5, $J_{H-H} = 7.5$ Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 9.94 (s, C_5Me_5), 55.79 (d, $P(OCH_3)_3$, $J_{C-P} = 7.8$ Hz), 101.91 (s, C_6H_5), 123.59 (s, p-C_6H_5), 127.08 (s, m-C_6H_5), 141.48 (s, o-C_6H_5), 221.30 (d, CO, $J_{C-P} = 34.0$ Hz). MS (EI, 12 eV): m/z 586 (M^+), 558 ($M^+ - CO$), 480 ($M^+ - CO - C_6H_6$).

Photolysis of $Cp^*Re(CO)(PMe_2Ph)(N_2)$ (4) in Chlorobenzene. A solution of the dimethylphenylphosphine dinitrogen complex **4** (50 mg, 0.096 mmol) in chlorobenzene (10 mL) was irradiated in a Pyrex tube for 13 min. An IR spectrum of the resulting yellow solution showed the total disappearance of the dinitrogen complex. After removal of the

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(30) Klahn-Oliva, A. H.; Sutton D. *Organometallics* **1989**, *8*, 198. For additional information on synthetic methods for these types of compounds see: (a) Cusanelli, A.; Sutton, D. *Organometallics* **1995**, *14*, 4651. (b) Cusanelli, A.; Sutton, D. *Organometallics* **1996**, *15*, 1457.

volatile materials under vacuum at room temperature, the remaining oily residue was redissolved in ca. 2 mL of benzene and filtered through a short neutral alumina column. Removal of the solvent under vacuum gave a pale yellow-red solid, which was recrystallized from benzene−hexane at 269 K to provide **9** in 80% yield (46 mg, 0.077 mmol). IR ($\mathrm{CH_2Cl_2}$): ν_{CO} 1867 $\mathrm{cm^{-1}}$. $^{1}\mathrm{H}$ NMR ($\mathrm{CDCl_3}$): δ 1.47 (s, 15H, $\mathrm{C_5Me_5}$), 2.02 (d, 3H, $\mathrm{PMe_2C_6H_5}$, $J_{\mathrm{H-P}} = 9.8$ Hz), 2.12 (d, 3H, $\mathrm{PMe_2C_6H_5}$, $J_{\mathrm{H-P}} = 9.8$ Hz), 6.97 (m, 1H, *p*-$\mathrm{C_6H_5}$, $J_{\mathrm{H-H}} = 7.0$ Hz), 7.10 (m, 2H, *m*-$\mathrm{C_6H_5}$, $J_{\mathrm{H-H}}$ 7.1 Hz), 7.8 (m, 3H, $\mathrm{PMe_2C_6}H_5$), 7.82 (m, 2H, $\mathrm{PMe_2C_6}H_5$, 7.96 (m, 2H, *o*-$\mathrm{C_6H_5}$, $J_{\mathrm{H-H}} = 6.8$ Hz, $J_{\mathrm{H-H}} = 1.2$ Hz). $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR ($\mathrm{CDCl_3}$): δ 10.13 (s, $\mathrm{C_5}Me_5$), 13.62 (d, $\mathrm{P}Me_2\mathrm{C_6H_5}$, $J_{\mathrm{C-P}} = 36.8$ Hz), 18.01 (d, $\mathrm{P}Me_2\mathrm{C_6H_5}$, $J_{\mathrm{C-P}} = 36.8$ Hz), 100.93 (s, $C_5\mathrm{Me_5}$), 123.40 (s, $C_6\mathrm{H_5}$ or $\mathrm{PMe_2}C_6\mathrm{H_5}$), 127.10 (s, $C_6\mathrm{H_5}$ or $\mathrm{PMe_2}C_6\mathrm{H_5}$), 128.30 (d, $C_6\mathrm{H_5}$ or $\mathrm{PMe_2}C_6\mathrm{H_5}$, $J_{\mathrm{C-P}} = 9.2$ Hz), 129.90 (br d, $C_6\mathrm{H_5}$ or $\mathrm{PMe_2}C_6\mathrm{H_5}$, $J_{\mathrm{C-P}} = 2.3$ Hz), 132.00 (d, $C_6\mathrm{H_5}$ or $\mathrm{PMe_2}C_6\mathrm{H_5}$, $J_{\mathrm{C-P}} = 7.6$ Hz), 136.76 (d, $C_6\mathrm{H_5}$ or $\mathrm{PMe_2}C_6\mathrm{H_5}$, $J_{\mathrm{C-P}} = 46.5$ Hz), 140.14 (d, $C_6\mathrm{H_5}$ or $\mathrm{PMe_2}C_6\mathrm{H_5}$, $J_{\mathrm{C-P}} = 10.7$ Hz), 142.18 (s, $C_6\mathrm{H_5}$ or $\mathrm{PMe_2}C_6\mathrm{H_5}$), 224.93 (d, CO, $J_{\mathrm{C-P}} = 24.0$ Hz). MS (EI): *m*/*z* 523 ($\mathrm{M^+} - \mathrm{C_6H_5}$). Anal. Calcd for $\mathrm{C_{25}H_{31}ClOPRe}$: C, 50.08; H, 5.22. Found: C, 50.19; H, 5.14.

Photolysis of Cp*Re(CO){P(OPh)$_3$}(N$_2$) (5) in Chlorobenzene. A solution of the triphenyl phosphite dinitrogen complex **5** (20 mg, 0.029 mmol) in chlorobenzene (6 mL) was irradiated in a Pyrex tube for 6 min. An IR spectrum of the resulting pale yellow solution showed the complete disappearance of the dinitrogen complex. Immediately after the irradiation, the volatile materials were removed under vacuum at room temperature and the resulting oily residue was taken up in $\mathrm{CDCl_3}$ without purification. A $^{1}\mathrm{H}$ NMR spectrum of this solution showed the only product to be the intramolecular C−H activation complex ***cis(P−H)*-10**. The solvent was then removed under vacuum at room temperature, and the remaining oily residue was redissolved in ca. 2 mL of benzene and filtered through a short neutral alumina column. Recrystallization from benzene−hexane at 269 K provided exclusively ***cis(P−H)*-10** in 80% yield (15 mg, 0.023 mmol). This product was shown from the following data to be identical with that synthesized and characterized in previous work.[19] IR($\mathrm{CH_2Cl_2}$): ν_{CO} 1927 $\mathrm{cm^{-1}}$. $^{1}\mathrm{H}$ NMR ($\mathrm{CDCl_3}$): δ −10.12 (d, 1H, ReH, $J_{\mathrm{P-H}} = 61.0$ Hz), 1.99 (s, 15H, $\mathrm{C_5Me_5}$), 6.80 (m, 3H, $\mathrm{OC_6H_5}$ or η^2-$\mathrm{OC_6H_4}$), 6.97 (m, 3H, $\mathrm{OC_6H_5}$ or η^2-$\mathrm{OC_6H_4}$) 7.12 (m, 2H, $\mathrm{OC_6H_5}$ or η^2-$\mathrm{OC_6H_4}$), 7.19 (m, 1H, $\mathrm{OC_6H_5}$ or η^2-$\mathrm{OC_6H_4}$), 7.34 (m, 1H, $\mathrm{OC_6H_5}$ or η^2-$\mathrm{OC_6H_4}$), 7.41 (m, 4H, $\mathrm{OC_6H_5}$ or η^2-$\mathrm{OC_6H_4}$)). MS (EI, 12 eV): *m*/*z* 660 ($\mathrm{M^+}$) 630 ($\mathrm{M^+} - \mathrm{CO} - 2\mathrm{H}$), 537 ($\mathrm{M^+} - \mathrm{CO} - 2\mathrm{H} - \mathrm{C_6H_5O}$).

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