Photochemical Reactions of the Rhenium Dinitrogen Phosphine and Phosphite Complexes Cp*Re(CO)(L)(N_2) (L = $P(OMe)_3$, $P(OEt)_3$, $P(OPh)_3$, $P(OCH_2)_3CCH_3$, PPh_3) in Hydrocarbon Solvents

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Results are reported for the UV photolysis of the rhenium dinitrogen phosphite and phosphine complexes Cp*Re(CO)(L)(N_2) (L = $P(OEt)_3$ (**1**), $P(OPh)_3$ (**2**), $P(OCH_2)_3CCH_3$ (**3**), $P(OMe)_3$ (**4**), PPh_3 (**5**)) in hydrocarbon solvents. Irradiation of **1** in hexane yielded cis and trans isomers of the cyclometalated complex Cp*Re(CO){η^2-$P(OCH_2CH_2)(OEt)_2$}H (**6**) and a third product identified as ***agostic*-6**, in which a methyl C−H bond of one of the ethoxy groups forms an agostic interaction with the metal. This complex decayed to give the other two isomers of **6** over time. Irradiation of **1** in benzene afforded the above compounds plus two isomers of a benzene C−H activation product Cp*Re(CO){$P(OEt)_3$}(Ph)H (**7**). The latter isomers and the agostic complex all decayed over time to leave only the cis and trans isomers of **6**. The final observed ratio of ***cis(P,H)*-6** to ***trans(P,H)*-6** was 76:24. Irradiation of **2** in hexane, cyclohexane, *or benzene* produced no evidence of any intermolecular C−H activation product. In each case, two products resulted, one of which was the cis(P,H) isomer of the orthometalated complex Cp*Re(CO){η^2-$P(OC_6H_4)(OPh)_2$}H (**8**) and the other of which was the agostic complex ***agostic*-8**, which slowly decayed away in favor of ***cis(P,H)*-8**. In a similar way, the triphenylphosphine complex **5** gave no observable benzene C−H activation product, and agostic and cis isomers of the intramolecular complex **11** were formed. These results indicate an overwhelming thermodynamic preference for cyclometalation over intermolecular C−H activation with these phosphorus ligands. The cage phosphite complex **3**, for which cyclometalation is hindered, gave an observable, but unstable, benzene C−H activation product **9** on irradiation in this solvent but no identifiable products when irradiated in hexane or cyclohexane. The product from irradiation of the trimethyl phosphite complex **4** in benzene, cyclohexane, or hexane is completely different from any of the above and does not result from C−H activation. It is formulated as the binuclear phosphonate complex [Cp*Re(CO){$PO(OMe)_2$}(CH_3)$]_2$ (**10**) involving methyl migration from a trimethyl phosphite ligand to the metal.

Introduction

In previous papers we have reported the results of the photolysis of the rhenium dinitrogen phosphine complexes Cp*Re(CO)(PMe_3)(N_2) and Cp*Re(CO)(PCy_3)(N_2) (Cy = cyclohexyl) in hydrocarbons.[1,2] Rapid loss of the dinitrogen ligand occurred, and the intermediate reacted with C−H bonds in an inter- or intramolecular fashion. Specifically, irradiation of Cp*Re(CO)(PMe_3)(N_2) in benzene produced the intermolecular C−H activation product *trans(C,H)*-Cp*Re(CO)(PMe_3)(Ph)H, whereas irradiation in cyclohexane provided only the cyclometalated product *trans(C,H)*-Cp*Re(CO){η^2-$P(CH_2)Me_2$}H. By way of contrast, irradiation of Cp*Re(CO)(PCy_3)(N_2) in cyclohexane *or benzene* gave only the orthometalated complex *cis(C,H)*-Cp*Re(CO){η^2-$P(C_6H_{10})Cy_2$}H.[2]

Noting the dependence of the photochemical products on the nature of the phosphine ligand as regards both the ability to activate the aromatic solvent and the stereochemistry of the cyclometalated product, we considered it worthwhile to extend these studies to a wider range of phosphorus coligands. In this paper, we describe the results obtained where the coligands are PPh_3 and various phosphites.

Results

1. Photolysis of Cp*Re(CO){$P(OEt)_3$}(N_2) (1) in Hexane. Photolysis of a hexane solution of Cp*Re(CO){$P(OEt)_3$}(N_2) **(1)** was carried out in a Pyrex vessel for 10 min. Spectroscopy indicated the formation of three products. Two are the cyclometalated complexes *trans*-

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(1) Klahn-Oliva, A. H.; Singer, R. D.; Sutton, D. *J. Am. Chem. Soc.* **1986**, *108*, 3107.
(2) Aramini, J. M.; Einstein, F. W. B.; Jones, R. H.; Klahn-Oliva, A. H.; Sutton, D. *J. Organomet. Chem.* **1990**, *385*, 73.

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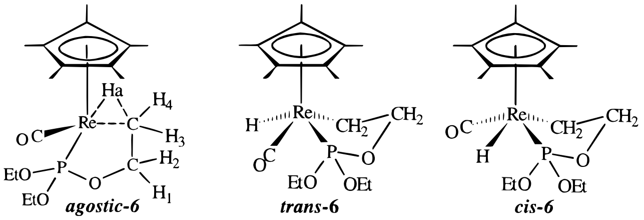
Chart 1. Proposed Structures for *trans*-6, *cis*-6, and *agostic*-6



(P,H)-Cp*Re(CO){η^2-P(OCH$_2$CH$_2$)(OEt)$_2$}H (***trans*-6**) and *cis(P,H)*-Cp*Re(CO){η^2-P(OCH$_2$CH$_2$)(OEt)$_2$}H (***cis*-6**) resulting from intramolecular C−H activation of an ethoxy group in the triethyl phosphite ligand. A third, the major product, has spectroscopic properties that indicate it to be an agostic complex, and we assign this as the complex ***agostic*-6** (Chart 1). Throughout this paper, cis and trans refer to the relative positions of P and H unless designated otherwise.

The IR spectrum after the photolysis showed two ν_{CO} bands at 1898 and 1860 cm^{-1}; subsequent work indicated that the band at 1860 cm^{-1} was associated with ***agostic*-6** (since this disappeared as ***agostic*-6** decayed) and the one at 1898 cm^{-1} with both ***cis*-6** and ***trans*-6** (since no new absorption appeared as the relative proportions of these isomers changed). After the solvent was removed at 273 K, the ^{1}H NMR spectrum of the crude photoproduct (recorded immediately in toluene-d_8 at 273 K) showed the disappearance of **1** and exhibited *three* resonances in the metal "hydride" region. The major resonance was a doublet at δ −9.82 with J_{PH} = 12.0 Hz assigned to ***agostic*-6**. The doublet at δ −10.10 with J_{PH} = 28.0 Hz was assigned to ***trans*-6**, and the one at δ −10.20 with J_{PH} = 60.0 Hz was assigned to ***cis*-6**. (J_{PH} coupling was confirmed by phosphorus decoupling). Subsequent work confirmed that these hydride resonances arise from separate products. The relative amounts of ***agostic*-6**:***trans*-6**:***cis*-6** were 66:26:7 by integration of these hydride resonances. Although the NMR spectra clearly showed the presence of hydride, no hydride IR absorptions were evident. The Cp* region showed three resonances at δ 1.86, 1.83, and 1.93. The methyl and methylene regions at δ 1.00−1.50 and 2.80−4.30 showed a complicated set of multiplets indicative, at least, of inequivalent triethyl phosphite ligands. The major product was further indicated to be ***agostic*-6** by immediately running an ^{1}H homonuclear chemical shift correlated (COSY) experiment at 273 K on this sample and by variable-temperature ^{1}H NMR spectra (273−313 K), both in toluene-d_8. Fortunately, several resonances for this complex were well separated from those of the other two products, which were present in smaller concentration, gave overlapping resonances, and were not easily characterized by the COSY. The COSY spectrum showed the presence of five inequivalent hydrogens for one of the ethoxy groups in the triethyl phosphite ligand of ***agostic*-6**. The resonances all integrated for one proton respectively and were mutually correlated. One resonance occurred at δ −9.92 and is assigned to the *agostic* hydrogen H$_a$. (This is considered to be the same resonance cited above at δ −9.82 for the crude product.) The other resonances at δ 1.49 and 2.84 are assigned to H$_3$ and H$_4$ (or vice versa) and those at δ 3.32 and 4.05 to H$_1$ and H$_2$ (or vice versa) in this ethoxy group (see Chart 1 for atom numbering). The resonance at δ −9.92 showed cross-peaks to the resonances at δ 1.49 and 2.84 (H$_3$ or H$_4$), the latter being the most intense. The resonances at δ 1.49 and 2.84 were correlated, and the one at δ 2.84 was also correlated with the resonance at δ 3.32. Finally, the resonances at δ 3.32 and 4.05 (H$_1$ or H$_2$) were correlated. Resonances for the remaining two ethoxy groups were assigned as indicated in the Experimental Section.

The assignment of the major product as an agostic complex, ***agostic*-6**, is made on the basis of its subsequent decay (see below), the observed reduced value (12 Hz) of the P−H coupling constant, and the result of the COSY experiment that shows a high-field "hydride" resonance significantly correlated to other protons of an ethoxy group. This assignment compares satisfactorily with those made previously for agostic ethyl or similar groups in cobalt[3] and molybdenum[4] complexes. As an example, for the complex Cp*Co{P(OMe)$_3$}(C$_2$H$_4$)H, the ^{1}H NMR spectrum showed a dynamic interconversion of the ethylene hydride complex with an alternative complex having an agostic ethyl ligand. The ^{1}H NMR spectrum at 203 K assigned to the agostic structure showed a hydride-like multiplet at δ −12.1 with a small value of J_{PH} = 12 Hz and the methylene hydrogens were inequivalent.[3b] A coincidentally identical value of J_{PH} is observed for ***agostic*-6**. This value can be compared to observed values of J_{PH} = ~27 Hz when the phosphorus ligand is trans to a true hydride and J_{PH} = ~69 Hz when the phosphorus ligand is cis to a true hydride in some four-legged piano stool molybdenum complexes, which serve as a reference for typical J_{PH} values to be expected for *terminal hydride* structures in similarly related rhenium complexes.[1,2,5] Therefore, the J_{PH} values observed for the hydride resonances at δ −10.10 and −10.20 in the present case, which are 28.0 and 60.0 Hz, respectively, readily allow these to be assigned to the complexes ***trans*-6** and ***cis*-6**. Other agostic complexes with a phosphine or phosphite ligand have displayed similar low J_{PH} couplings, and these are interpreted to be an indication of a reduced M−H bond order in the 3-center−2-electron interaction.[3b,6] The total remaining six OEt groups in ***agostic*-6**, ***cis*-6**, and ***trans*-6** are all inequivalent, leading to the complexity of the methyl and methylene regions. Partial assignments were made from changes in relative intensities (see below) and coupling patterns where these could be seen.

2. Variable-Temperature ^{1}H NMR Data for Isomers of 6 in Toluene-d_8. The purpose of these experiments was to examine in more detail whether there is any interconversion of the agostic, trans, and cis isomers of **6**. First, an ^{1}H NMR spectrum was acquired at 273 K, 1.55 h after the above COSY experiment. This showed that some change had occurred over time while the temperature had remained

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(3) (a) Schmidt, G. F.; Brookhart, M. *J. Am. Chem. Soc.* **1985**, *107*, 1443. (b) Brookhart, M.; Lincoln, D. M.; Volpe, A. F., Jr.; Schmidt, G. F. *Organometallics* **1989**, *8*, 1212. (c) Brookhart, M.; Volpe, A. F., Jr.; Lincoln, D. M.; Horvath, I. T.; Miller, J. M. *J. Am. Chem. Soc.* **1990**, *112*, 5634.

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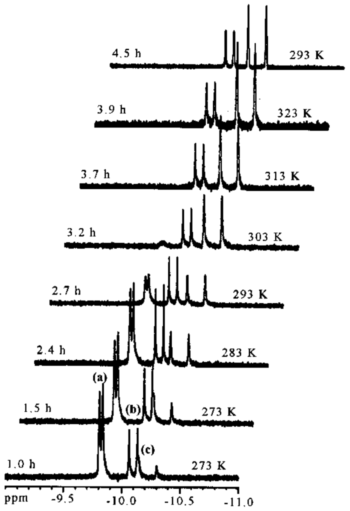

Figure 1. Variable-temperature ^{1}H NMR spectra for the isomers of **6** in toluene-d_8 in the hydride region (for data see Table 1): (a) ***agostic*-6**; (b) ***trans*-6**; (c) ***cis*-6**.

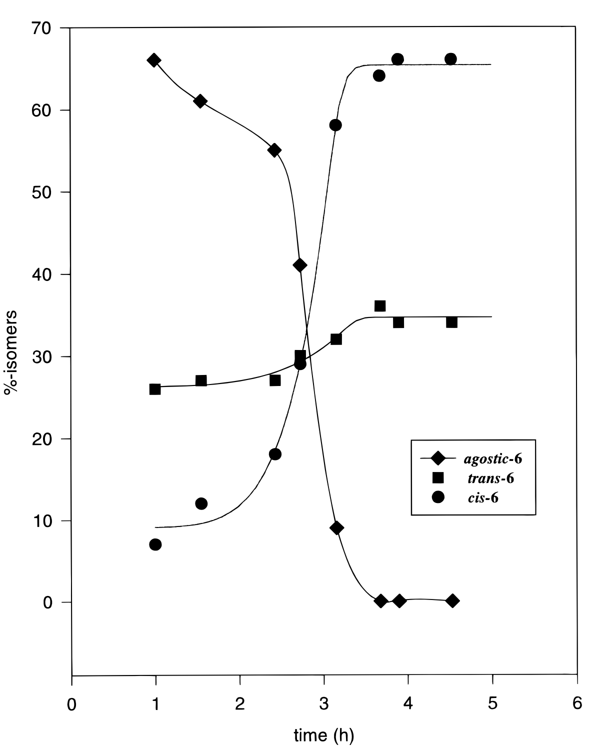

Figure 2. Distribution of species plot of the data in Table 1. (Note that the temperature is not constant throughout.)

constant and that the intensity of the resonance at δ -9.83 characteristic of ***agostic*-6** was decreasing. Further spectra were recorded from 283 to 303 K over about 3 h, with the result that the proportion of ***agostic*-6** decreased but also the ratio of trans and cis isomers changed (Figures 1 and 2 and Table 1). When the temperature was increased to 313 K, the signal at δ -9.83 disappeared, with the concomitant growth of the cis and trans isomers. The temperature was raised to 323 K, and the ratio of the remaining cis and trans isomers changed slightly. The sample was then cooled to 293 K and stored at this temperature for 0.63 h. The ratio of the two isomers remained the same by NMR spectroscopy. The final ratio of ***trans*-6**:***cis*-6** after the variable-temperature study was 34:66.

The changes in relative proportions of ***trans*-6** and ***cis*-6** facilitated unique assignments of the Cp* and some of the phosphite ethoxy resonances of these isomers. Observable resonances corresponding to the cyclometalated group (η^2-$POCH_2CH_2$) for ***cis*-6** were at δ 2.39 (relative integral 1H) and δ 3.40 (relative integral 2H). Specific resonances were not assignable in the ^{1}H spectrum at 293 K for the cyclometalated group in the now less abundant ***trans*-6**.

Unstable alkyl or aryl hydride complexes can generally be converted to more stable halide complexes by adding halogenated solvents, so as to facilitate isolation and identification.[7,8] Attempts to do this with **6** and CCl_4 or $CHCl_3$ did not afford the corresponding cyclometalated complex Cp*Re(CO)\{η^2-P(OCH_2CH_2)($OEt)_2$\}-Cl. Instead, the only species detectable was *trans*-Cp*Re(CO)\{P($OEt)_3$\}Cl_2,[9a] identified from MS and IR ν_{CO} data.[9b]

3. Isomerization of *agostic*-6 to *cis*-6 and *trans*-6 at Room Temperature. The crude product from a fresh photolysis of Cp*Re(CO)\{P($OEt)_3$\}(N_2) (**1**) in hexane was dried under vacuum and dissolved in benzene-d_6, and the ^{1}H NMR spectrum was recorded immediately. Resonances at δ 1.88, 1.89, and 1.91 were assigned to the presence of three different Cp* groups, and three doublet resonances were present in the metal hydride region. These resonances were reminiscent of those obtained in the above work and were assigned similarly: δ -10.11 ($J_{PH} = 62.0$ Hz) (***cis*-6**), δ -9.87 ($J_{PH} = 28.0$ Hz) (***trans*-6**), and δ -9.67 ($J_{PH} = 11.0$ Hz) (***agostic*-6**). These had relative intensity 19:38:43, respectively, and appeared as singlets upon phosphorus decoupling. The ^{31}P NMR spectrum of this crude photoproduct in benzene-d_6 at ambient temperature showed three different resonances for the phosphite ligands that could be assigned on the basis of the P$-$H couplings. Resonances at δ 158.8 and 46.6 with $J_{PH} =$ 58.8 and 27.0 Hz, respectively, were readily assigned to ***cis*-6** and ***trans*-6**. A broad singlet at δ 163.9 was assigned to ***agostic*-6**. The expected 11 Hz coupling was not resolved.

The isomerization of **6** was followed by ^{1}H NMR and ^{31}P NMR spectroscopies. The ^{1}H NMR resonance for ***agostic*-6** decreased to zero after 3 h, and the ratio of the other isomers was now trans:cis = 41:59. The spectrum after 24 h was almost the same, but the ratio of ***trans*-6** to ***cis*-6** finally recorded after ~96 h was 27:73.

4. Photolysis of Cp*Re(CO)\{P(OEt)$_3$\}(N$_2$) (1) in Benzene. A benzene solution of **1** was photolyzed in a Pyrex vessel for 8 min. IR spectroscopy showed a decrease in intensity of the ν_{CO} of **1** and a new broad band at 1885 cm^{-1} was the only new ν_{CO} absorption observed. The solvent-suppressed ^{1}H NMR spectrum showed apparently four resonances in the Cp* region and four doublets in the hydride region. The Cp* resonances could not be reliably assigned from relative intensities because of possible perturbation from their

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(7) Janowicz, A. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 3929.

(8) Periana, R. A.; Bergman, R. G. *Organometallics*, **1984**, *3*, 508.

(9) (a) Klahn-Oliva, A. H. Personal communication. Characterizing data are as follows. (b) For Cp*Re(CO)\{P($OEt)_3$\}Cl_2: IR (C_6H_6) ν_{CO} 1925 cm^{-1}; MS (EI, 12 eV) *m/z* 586 (M^+), 558 ($M^+ -$ CO). (c) For Cp*Re(CO)(Pc)Cl_2: IR (C_6H_6) ν_{CO} 1942 cm^{-1}; MS (EI, 12 eV) *m/z* 568 (M^+), 540 ($M^+ -$ CO).

Table 1. Variable-Temperature ^{1}H NMR Data for the Isomers Produced from the Photochemical Reaction of Cp*Re(CO){P(OEt)$_3$}(N$_2$) in Hexane

		isomer[a]					
		***agostic*-6**		***trans*-6**		***cis*-6**	
T (K)	time (h)	δ(Rh−H)	%	δ(Re−H)	%	δ(Re−H)	%
273	1.00	−9.83	66	−10.11	26	−10.20	7
273	1.55	−9.81	61	−10.11	27	−10.20	12
283	2.43	−9.83	55	−10.07	27	−10.24	18
293	2.73	−9.84	41	−10.06	30	−10.26	29
303	3.16	−9.83	9	−10.06	32	−10.27	58
313	3.68			−10.03	36	−10.28	64
323	3.90			−9.99	34	−10.28	66
293	4.53			−9.98	34	−10.28	66

[a] The ^{1}H NMR spectrum was recorded in toluene-d_8. The percentages of the isomers were obtained according to the intensities of the hydride resonances.

proximity to the benzene solvent resonance that was being irradiated but were assigned later on the basis of the intensities of the species growing or decreasing with time. The hydride resonances at δ −9.50, −9.67, and −9.93 could be immediately assigned respectively to the presence of ***agostic*-6**, ***trans*-6**, and ***cis*-6** on the basis of the chemical shift and J_{PH} by comparison with the above results. The fourth (and most intense) doublet in the hydride region, at δ −9.16 with $J_{PH} = 69.2$ Hz, was assigned to an isomer (***cis*-7**) of a benzene C−H activation product Cp*Re(CO){P(OEt)$_3$}(Ph)H (**7**) in which P and H are mutually cis, on the basis of further work (see below) and the value of J_{PH}. Subsequent observation of the decay of this spectrum indicated that the doublet at δ −9.67 assigned to ***trans*-6**, is almost coincident with another similar doublet which occurs at δ −9.66 with $J_{PH} = 28.0$ Hz which we assign to the presence of the isomer of **7** having P and H mutually trans (***trans*-7**).

The spectrum changed significantly in the following 2 h. The resonances for ***agostic*-6** and ***cis*-7** disappeared, but that for ***cis*-6** increased and there was a change in the situation at ca. δ −9.67 which was interpreted as a loss of ***trans*-7** and increase in ***trans*-6**. This interpretation was later substantiated by the results of a time-dependent study in benzene-d_6. The variation in intensity of the hydride signal of ***cis*-7** allowed a partial assignment of two similarly varying methyl resonances at δ 1.19 and 1.27 and two methylene multiplets at δ 3.90 and 4.11 to the ethoxy groups of this complex. No specific resonances were assignable for the other isomers.

5. Photolysis of Cp*Re(CO){P(OEt)$_3$}(N$_2$) (1) in Benzene-d_6. From the results for the irradiation of **1** in benzene described in the last section, it was concluded that two of the products (***cis*-7** and ***trans*-7**) had resulted from the C−H activation of benzene. This could be tested by carrying out the irradiation in benzene-d_6, in which case the corresponding hydride resonances should be absent. A benzene-d_6 solution of **1** in a Pyrex vessel was irradiated for 12 min. An ^{1}H NMR spectrum of the crude sample recorded immediately showed almost complete disappearance of **1**, *five* resonances in the Cp* region, and *three* in the metal hydride region. The hydride signals were immediately assignable to the cyclometalated C−H activation products ***trans*-6**, ***cis*-6**, and ***agostic*-6** on the basis of the foregoing results. The absence of a fourth hydride (i.e., near δ −9.16) immediately indicated that this signal assigned in the previous section to ***cis*-7** indeed results from the activation of benzene. Also, the much smaller intensity observed now for the doublet assigned to ***trans*-6** is support for the contention in the previous section that this doublet had a contribution from ***trans*-7**. As will be seen next, this contention receives additional support when the ^{31}P NMR spectrum is analyzed.

The ^{31}P NMR spectrum of this sample, taken immediately after the ^{1}H spectrum, showed *five* distinguishable resonances at δ 160.0, 156.8, 122.2, 116.5, and 42.6. The ^{31}P NMR resonances at δ 160.0, 156.8, and 42.6 are in agreement with the resonances observed previously for ***agostic*-6**, ***cis*-6**, and ***trans*-6** obtained from the photolysis of **1** in hexane. The two other ^{31}P resonances at δ 122.3 and 116.5 are therefore assigned to ***cis*-7-*d*$_6$** and ***trans*-7-*d*$_6$**, respectively. The assignment of the downfield-shifted resonance at δ 122.3 to a phosphorus which is cis with respect to D and the one at δ 116.5 to a phosphorus which is trans with respect to D is based on a comparison with the ^{31}P{^{1}H} NMR spectra for isomers of [Cp*Re(CO)$_2$LX]$^+$ (L = P(OMe)$_3$, P(OEt)$_3$; X = Cl, Br, I) where trans (P−CO) was observed downfield compared with the cis (P−CO) isomer.[10] It was observed in the ^{1}H NMR spectrum reported above that ***cis*-7** showed a larger J_{PH} coupling than ***trans*-7**. We now expected the same situation for the J_{PD} coupling in ^{31}P NMR spectra. The resonances for **7-*d*$_6$** were broad but J_{PD} coupling was not resolved; however, the resonance at δ 122.3 was indeed broader than the one at δ 116.5. The ^{31}P NMR intensities further show that the major isomer present is ***cis*-7-*d*$_6$**. This is consistent with the ^{1}H NMR spectrum, where ***cis*-7** was the major product. Although, from the above data, ***cis*-7** is identified to have P and H(D) atoms in a cis arrangement, the available data do not allow us to distinguish which of the two possible configurations in Chart 2 is correct.

The evolution of this mixture as a function of time over 45 h was traced by measuring the ^{1}H and ^{31}P NMR spectra on the sample at regular intervals. The resonances assigned to ***agostic*-6** and those assigned to ***cis*-7-*d*$_6$** and ***trans*-7-*d*$_6$** gradually disappeared (for ***cis*-7-*d*$_6$** and ***trans*-7-*d*$_6$**, this was best seen in the ^{1}H NMR spectra from the decrease in intensity of the Cp* signal), and those for ***cis*-6** and ***trans*-6** increased. The ratio of ***trans*-6** to ***cis*-6** appeared to stay reasonably constant

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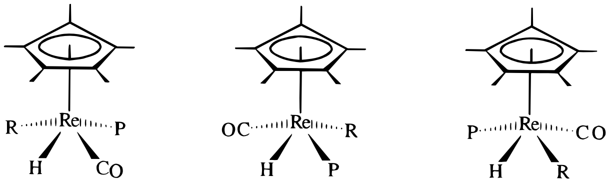
(10) Leiva, C.; Mossert, K.; Klahn-Oliva, A. H.; Sutton, D. *J. Organomet. Chem.* **1994**, *469*, 69.

Chart 2. Proposed Structures for Isomers of 7 (R = Ph) and Cp*Re(CO){P(OEt)$_3$}(C$_6$D$_5$)(D) (7-d_6) (R = C$_6$D$_5$, H = D): I, *trans(P,D(H))*; II or III, *cis(P,H(D))*

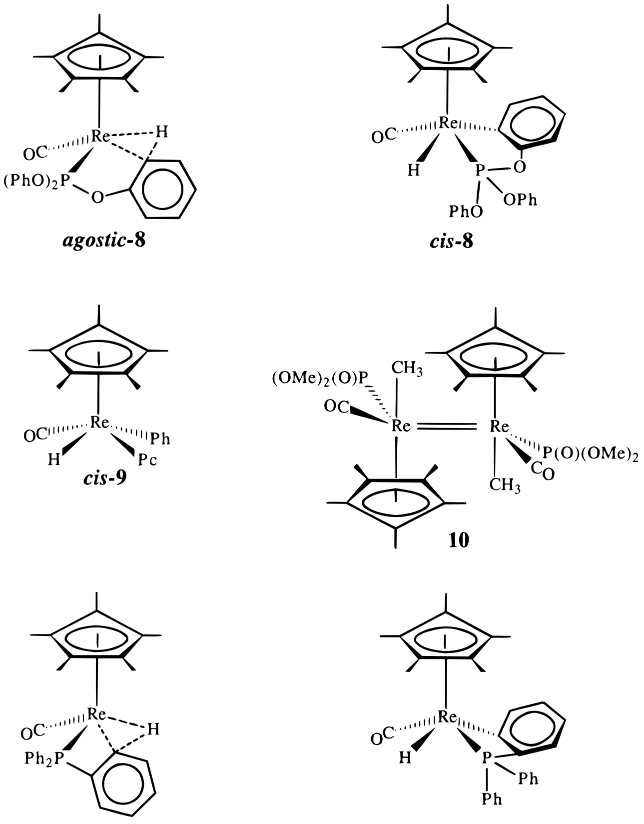


I trans **II** cis **III** cis

from ca. 3 to 21 h, and the ratio of ca. 33:67 is similar to that observed in section 2 at a similar time, but a spectrum after 45 h showed that ***cis*-6** had increased further relative to ***trans*-6** (ratio 24:76). This is very similar to the ratio finally observed in section 3, but we cannot be sure that this represents a final equilibrium ratio.

6. Photolysis of Cp*Re(CO){P(OPh)$_3$}(N$_2$) (2) in Benzene, Hexane, or Cyclohexane. Irradiation of the triphenyl phosphite dinitrogen complex **2** in benzene, cyclohexane, or hexane in a Pyrex vessel for 9 min in all cases gave the intramolecular C−H activation product Cp*Re(CO){η^2-P(OC$_6$H$_4$)(OPh)$_2$}H (**8**). The orthometalated complex **8** was isolated from benzene−hexane (1:1) at 258 K as a pale yellow solid and was characterized spectroscopically. Complex **8** was stable under nitrogen and was soluble in benzene, toluene, and cyclohexane and slightly soluble in hexane. The IR spectrum of **8** showed a strong ν_{CO} absorption at 1946 cm^{-1} in hexane but no detectable absorption corresponding to a metal hydride vibration. The ^{1}H NMR spectrum in acetone-d_6 exhibited a singlet resonance corresponding to Cp*, and the phenyl groups of the phosphite ligand gave a set of multiplets with a relative integrated area of 14H. The identification of the different proton resonances of the η^2-P(OC$_6$H$_4$)(OPh)$_2$ group was difficult due to the inequivalent phenyl rings. The spectrum also exhibited a doublet in the metal hydride region at δ −10.09 with a relative integrated area of 1H and J_{PH} = 63.0 Hz, indicating cis hydride and phosphorus ligands. The ^{13}C{^{1}H}NMR spectrum of **8** in benzene-d_6 showed resonances for the triphenyl phosphite moiety in the δ 110−163 region, but the assignment of the different carbons in the triphenyl phosphite ligand was obscured due to overlapping resonances. The carbonyl carbon resonance was observed at δ 202.4 as a doublet from coupling to phosphorus with J_{PC} = 15.0 Hz. The value suggests that the carbonyl ligand is trans to the phosphorus.[11] The ^{31}P{^{1}H}NMR spectrum of **8** in acetone-d_6 exhibited a single resonance at δ 83.49. These results suggest that the isolated product **8** has the structure shown in Chart 3, i.e., ***cis(P,H)*-8**. The electron-impact (EI) mass spectrum confirmed the formulation of **8**. It showed the molecular ion at *m*/*z* 630 and a base peak at *m*/*z* 600 corresponding to the loss of CO and 2H. The loss of two H atoms from the C$_5$Me$_5$ ligand in the fragmentation of Cp* complexes is well documented.[12]

Chart 3. Proposed Structures for *cis*-8, *agostic*-8, *cis*-9, 10, *cis*-11, and *agostic*-11



agostic-**8** *cis*-**8** *cis*-**9** **10** *agostic*-**11** *cis*-**11**

While the hydride complexes **6** and **7** described above were rather unstable, typical of many metal hydride complexes arising from C−H activation reactions, ***cis*-8** was found to be stable in the solid state and in solution. Furthermore, treatment of ***cis*-8** with chloroform-*d* at room temperature showed no evidence of formation of the analogous chloro complex and ***cis*-8** was unchanged.

7. Photolysis of Cp*Re(CO){P(OPh)$_3$}(N$_2$) (2) in Benzene-d_6. From the irradiation of **2** in benzene, only ***cis*-8** was observed as the isolated final product. The purpose of this experiment, therefore, was to examine in detail by in situ ^{1}H NMR spectroscopy at relatively short times the possible formation of other, shorter-lived, products.

A benzene-d_6 solution of **2** in a Pyrex vessel was irradiated for only 5 min. An ^{1}H NMR spectrum of the solution recorded immediately after the irradiation showed almost complete disappearance of **2**. The spectrum exhibited two doublets in the metal hydride region. The combined integration was $^1/_{15}$ the intensity of the single Cp* resonance observed at δ 1.84, and the integration of the phenyl multiplets at δ 6.79−7.46 was consistent with the Cp* integration. The hydride resonance at δ −9.78 was a doublet with J_{PH} = 62.9 Hz, consistent with a cis arrangement of hydride and adjacent phosphite ligand.[5] This is assigned to ***cis*-8**. The signal at δ −7.95 was a doublet with a coupling constant of 11.0 Hz. Because of the small coupling constant, this was assigned to the presence of ***agostic*-8** by comparison with the results reported above for

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***agostic*-6**. The ^{1}H NMR spectrum of the same sample acquired after 3.5 h showed a large decrease in the hydride resonance at δ −7.95 for ***agostic*-8** and the concomitant growth of ***cis*-8** with respect to the remaining unreacted **2**.

8. Photolysis of Cp*Re(CO)(Pc)(N$_2$) (3) in Hexane. In the irradiation of **1** in hexane, two products (***cis*-6** and ***trans*-6**) were observed that resulted from the C−H activation of an ethoxy group in the triethyl phosphite ligand. To minimize the possibility of a cyclometalated product, and thus possibly allow formation of an intermolecular alkane C−H activation product to be promoted, we investigated the photolysis of Cp*Re(CO)(Pc)(N$_2$) (**3**). The Pc ligand $P(OCH_2)_3CCH_3$ has electronic properties similar to those of $P(OEt)_3$ and $P(OMe)_3$, but its structure precludes cyclometalation.

A hexane solution of **3** in a Pyrex vessel was irradiated for 10 min. The reaction was followed by IR spectroscopy every 3 min. No evidence of any new ν_{CO} absorption was detected, and the original ν_{CO} and ν_{N_2} absorptions disappeared. The solvent was removed, and the residue (without purification) was dissolved in benzene-d_6. The ^{1}H NMR spectrum showed no evidence of any C−H activation product (i.e., no hydride resonances) or resonances assignable to the Cp* ligand.

9. Photolysis of Cp*Re(CO)(Pc)(N$_2$) (3) in Benzene. A benzene solution of **3** was irradiated in a Pyrex vessel for 10 min. The reaction was followed by IR spectroscopy, and the starting material showed a decrease in intensity of the original absorptions at ν_{N_2} 2079 and ν_{CO} 1880 cm^{-1}, and a new ν_{CO} at 1913 cm^{-1} was observed. A solvent-suppressed ^{1}H NMR spectrum of the solution after the irradiation indicated the complete disappearance of **3** and the apparent formation of a C−H activation product. The ^{1}H NMR spectrum showed a resonance at δ −0.50 integrating for 3H and a resonance at δ 3.34 integrating for 6H which were assigned to the Pc ligand and a resonance for Cp* at δ 1.72 integrating for 15 H. A doublet (J_{PH} = 68.8 Hz) in the metal hydride region at δ −9.20 integrated for 1 H. This product is formulated as *cis(P,H)*-Cp*Re(CO)(Pc)(C_6H_5)H (***cis*-9**) (see Chart 3).

An ^{1}H NMR spectrum of the same sample was acquired after 1 h at room temperature and showed a decay of the product. This complex proved difficult to fully characterize spectroscopically due to its thermal instability at room temperature as demonstrated by the ^{1}H NMR spectrum. An attempt to convert the phenyl hydride complex **9** to a possibly more stable phenyl halide complex by reaction with CH_3Cl or CCl_4 failed. The only species observed was the dihalide complex Cp*Re(CO)(Pc)Cl$_2$, identified from the IR and mass spectra.[9a,c]

10. Photolysis of Cp*Re(CO){P(OMe)$_3$}(N$_2$) (4) in Hexane, Cyclohexane, or Benzene. A benzene solution of **4** in a Pyrex vessel was irradiated for 15 min. An ^{1}H NMR spectrum of the crude sample recorded in benzene-d_6 immediately after irradiation showed the complete disappearance of **4**, and the lack of any hydride resonances suggested there was no formation of any C−H activation products. The product (**10**) was purified by chromatography, recrystallized from hexane at 265 K as a pale yellow solid, and spectroscopically characterized. Photolysis of **4** in hexane or cyclohexane gave analogous results.

The IR spectrum of **10** showed *two* ν_{CO} absorptions at 1900 and 1879 cm^{-1} with similar intensity. The ^{1}H NMR spectrum in acetone-d_6 exhibited one singlet resonance for Cp* integrating to 15H and two doublets at δ 3.42 and 3.49 (integral 6H) for the diastereotopic phosphonate OMe protons with J_{PH} = 8.0 Hz. The ^{1}H NMR spectrum showed a resonance at δ 0.74 (integral 3H) which was assigned to a methyl group coordinated to the rhenium.

The ^{13}C{^{1}H} NMR spectrum of **10** in acetone-d_6 also demonstrated the presence of a metal-bound methyl group at δ −0.98 (J_{CP} = 11.7 Hz) and two inequivalent methyl groups of the phosphonate ligand at δ 51.35 and 52.66 with J_{CP} = 11.4 Hz. The carbonyl carbon resonance was observed at δ 221.35 as a doublet with J_{CP} = 28.9 Hz. The ^{31}P{^{1}H} NMR spectrum of **10** in acetone-d_6 exhibited a single resonance at δ 80.70. This chemical shift is typical for a coordinated phosphonate group.[10] The formulation of **10** as a binuclear complex was made on the basis of the electron impact (EI) spectrum, which showed a dirhenium isotopic pattern assignable to the molecular ion at *m/z* 946 and a base peak at *m/z* 918, resulting from the loss of a carbonyl ligand, having a similar pattern. The tentatively proposed structure for **10** that is in accord with the spectroscopic data is shown in Chart 3.

The proposed stereochemistry for **10** is based upon the observation of a single resonance in the ^{1}H NMR spectrum for the Cp* ligands (which must be symmetry-related), and the situation is similar for the rhenium methyl groups. The single resonance observed for the phosphonate phosphorus in the ^{31}P{^{1}H} NMR spectrum and observation of only two diastereotopic OMe groups indicate that the phosphonate ligands are also symmetry-related. However, the presence of two ν_{CO} IR absorbances indicates that the CO groups are not centrosymmetric. The configuration shown in Chart 3 in which the individual Cp*, CH_3, phosphonate, and CO groups are 2-fold related appears to satisfactorily fit the observed data. The proposed formal Re=Re double bond is required to fulfill an 18-electron count for each Re. So far, all attempts to obtain an X-ray structure for this complex have failed because of the poor quality of the crystals obtained.

11. Photolysis of Cp*Re(CO)(PPh$_3$)(N$_2$) (5) in Benzene, Hexane, Cyclohexane, or Benzene-d_6. The solvent-suppressed ^{1}H NMR spectrum of the crude solution obtained after photolysis of **5** in benzene in a Pyrex vessel for 10 min exhibited two singlet resonances at δ 1.69 and 1.78, which were assigned to Cp* ligands. In the metal hydride region were two sets of doublets at δ −7.55 and −7.98 with J_{PH} = 12.0 and 73.0 Hz, respectively. The resonance at δ −7.55 was assigned to ***agostic*-11** (Chart 3) on the basis of the size of the coupling constant. The other product was assigned as the cyclometalated complex *cis(P,H)*-Cp*Re(CO){η^2-P(C_6H_4)(C_6H_5)$_2$}H (***cis*-11**) resulting from the intramolecular C−H activation of one of the phenyl groups in the triphenylphosphine ligand (Chart 3). Photolysis of **5** in hexane, cyclohexane, or benzene-d_6 gave results comparable with those from the photolysis in benzene.

As an example, after the photolysis of **5** in cyclohexane the ^{1}H NMR spectrum of the solution showed a hydride signal at δ −8.53 with a coupling constant of 11.0 Hz assigned to ***agostic*-11** and a set of multiplets in the range δ 6.5−7.5 corresponding to the aromatic protons. The Cp* resonance is, of course, obscured by cyclohexane solvent suppression. The NMR spectra showed that ***agostic*-11** converted to the orthometalated complex ***cis*-11** over a period of 1 h at room temperature under nitrogen. Complex ***cis*-11** reacted with $CDCl_3$ or $CHCl_3$ (ca. 2 h) at room temperature to give an orange-yellow solution from which was obtained a solid product which was assigned by ^{1}H NMR, $^{13}C\{^1H\}$ NMR, and mass spectroscopies to be the corresponding chloro orthometalated complex *cis(P,Cl)*-$Cp^*Re(CO)\{\eta^2\text{-}P(C_6H_4)(C_6H_5)_2\}Cl$ (***cis*-12**). The ^{1}H NMR spectrum of ***cis*-12** exhibited a singlet at δ 1.53 (integrating to 15H) and a set of multiplets in the range δ 6.90−7.30 (integrating to 14H) which were assigned to Cp* and η^2-$P(C_6H_4)Ph_2$ moieties, respectively. The $^{13}C\{^1H\}$ NMR spectrum for **12** showed the presence of the Cp* and η^2-$P(C_6H_4)Ph_2$ ligands. The carbonyl carbon resonance was observed at δ 209.6 as a singlet. The unobservable coupling constant involving the phosphine ligand and the carbonyl moiety suggests that the phosphine in this complex is trans to the carbonyl group.[11] The formulation of **12** was corroborated by low-voltage electron impact (EI) mass spectroscopy at 12 eV, which showed the molecular ion at *m/z* 646 based on ^{187}Re and ^{35}Cl and a base peak at *m/z* 616 from loss of CO, both having the correct isotopic pattern.

Discussion

The results described here, when added to the relatively little previous work that has been done on the photolysis of $CpRe(CO)_3$, $Cp^*Re(CO)_3$, or their derivatives, show that the outcome is very sensitive to the identity of the coligand. Pasman et al. showed that irradiation of $Cp^*Re(CO)_3$ in benzene led to the formation of the rhenium η^2-benzene complex $Cp^*Re(CO)_2(\eta^2\text{-}C_6H_6)$.[13] No C−H bond activation of benzene was observed. A similar result was obtained when the dicarbonyl dinitrogen complex was irradiated in the same solvent.[14] Photolysis of $Cp^*Re(CO)_3$[15] or $Cp^*Re(CO)_2(N_2)$[14] in cyclohexane also did not yield any C−H activation product but gave $(Cp^*)_2Re_2(CO)_5$ and $(Cp^*)_2Re_2(CO)_3$.

However, by substituting one or more CO ligands by PMe_3, Bergman et al.[16,17] achieved C−H bond activation reactions. The complexes $CpRe(PMe_3)_3$ or $Cp^*Re(L)(PMe_3)_2$ (L = CO, PMe_3) gave isolable products arising from either cyclometalation or intermolecular C−H bond activation, and competition between the two processes was observed. The Cp* complexes differed in the results obtained with alkanes or cycloalkanes compared to the Cp ones. For Cp, C−H activation of these aliphatics was observed, but for Cp*, the product was only the cyclometalated complex $Cp^*Re(L)\{\eta^2\text{-}PCH_2(Me)_2\}H$ (L = CO, PMe_3). Notably, it was observed that the cyclometalated complexes in the Cp and Cp* systems react with benzene to produce $CpRe(PMe_3)_2(Ph)H$ or $Cp^*Re(L)(PMe_3)(Ph)H$ (L = CO, PMe_3) in equilibrium with the above cyclometalated product.

In our laboratory,[1,2] we subsequently studied the C−H activation of hydrocarbons with the related rhenium dinitrogen complexes $Cp^*Re(CO)(L)(N_2)$ (L = PMe_3, PCy_3). It was found that the irradiation time required for the loss of N_2 in the dinitrogen complexes was much shorter (ca. 5−10 min) when compared with the case of CO or PMe_3 ligands. The results obtained for the photolysis of $Cp^*Re(CO)(PMe_3)(N_2)$ in benzene were otherwise in agreement with the results reported earlier by Bergman.[16] Similarly, the photolysis of the trimethylphosphine complex in hexane or cyclohexane provided only the cyclometalated complex $Cp^*Re(CO)\{\eta^2\text{-}PCH_2(Me)_2\}H$ as had been reported by Bergman,[16] and when this complex was dissolved in C_6H_6 or C_6D_6, it converted to the intermolecular product $Cp^*Re(CO)(PMe_3)(Ph)H$.[1,2] Of interest, however, was our observation that irradiation of $Cp^*Re(CO)(PCy_3)(N_2)$ in cyclohexane *or benzene* provided only the intramolecular C−H activation product $Cp^*Re(CO)\{\eta^2\text{-}P(C_6H_{11})(Cy_2)\}H$, and no evidence for the activation of benzene was observed.[2]

To summarize the results now obtained with the rhenium dinitrogen phosphite and PPh_3 complexes $Cp^*Re(CO)(L)(N_2)$ (L = $P(OEt)_3$ (**1**), $P(OPh)_3$ (**2**), PPh_3 (**5**)), all of these gave the intramolecular cyclometalated C−H activation complex as the ultimate product after irradiation with hydrocarbons. For **1** both inter- and intramolecular C−H activation was observed when the complex was irradiated in C_6H_6. However, the intramolecular product was the thermodynamically preferred one. For the complex $Cp^*Re(CO)(Pc)(N_2)$ (**3**), where cyclometalation is hindered, an intermolecular benzene C−H activation product was obtained. In the cases of complexes **2** and **5** bearing triphenyl phosphite and triphenylphosphine ligands, respectively, the known tendency for cyclometalation[18] of a phenyl ring appeared to be overwhelming, and no product of intermolecular activation of benzene was observed at any point.

It is very instructive to compare the results of irradiation of the trimethyl phosphite complex $Cp^*Re(CO)\{P(OMe)_3\}(N_2)$ (**4**) with those of the trimethylphosphine work performed earlier and mentioned above. From the irradiation of **4** in hydrocarbons no evidence was observed for any C−H activation product at all. Instead, methyl migration of one of the $P(OMe)_3$ methyl groups to the rhenium center has occurred, and is discussed further below.

There are also some interesting stereochemical differences in the cyclometalated products depending on the ligand. The triethyl phosphite complex **1** generated isomers of the intramolecular C−H activation complexes, i.e., *trans*- and *cis*-$Cp^*Re\{\eta^2\text{-}P(OCH_2CH_2)(OEt)_2\}H$ (**6**). The analogous complexes with $P(OPh)_3$ (**2**) and PPh_3 (**5**) generated only one isomer of the

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cyclometalated products, *cis*-Cp*Re{η^2-P(OC_6H_4)($OPh)_2$}H (**8**) and *cis*-Cp*Re{η^2-P(C_6H_4)Ph_2}H (**11**), respectively.

The most notable result obtained in this study is the evidence for the intermediacy of persistent, recognizable, *agostic* complexes ***agostic*-6**, ***agostic*-8**, and ***agostic*-11**, respectively, on the route to cyclometalation in the cases of **1**, **2**, and **5**. Evidence to support these structures was (i) a resonance in the metal hydride region that has a small coupling constant (J_{PH} = ~12 Hz) which is not typical[5] for a classical metal hydride, (ii) a COSY NMR experiment performed on a mixture of ***cis*-6**, ***trans*-6**, and ***agostic*-6**, (iii) their observation only at short irradiation times, and (iv) their decay to the relatively more stable cyclometalated products.

The product from the irradiation of the trimethyl phosphite complex **4** is formulated as the binuclear complex [Cp*Re(CO){PO($OMe)_2$}(CH_3)]$_2$ (**10**) in which a methyl group has migrated to the rhenium center, presumably by an Arbuzov-like rearrangement.[19] In contrast to the other phosphites, no cyclometalated trimethyl phosphite complex was observed. This could be related with the relative instability of the four-membered ring required in this case.[20] Most Arbuzov-like rearrangements involving transition metal phosphite complexes are brought about by nucleophiles, and both ionic and radical mechanisms have been proposed. However, there are some examples of methyl migration involving a phosphite ligand which are difficult to categorize under these mechanisms. As an example, the thermolysis of Ru{(P($OMe)_3$}$_5$ produces the phosphonate complex Ru{P($OMe)_4$}{PO($OMe)_2$}Me.[21] Inhibition of this rearrangement by the presence of free P($OMe)_3$ suggested that an equilibrium involving dissociation to Ru{(P($OMe)_3$}$_4$ may be involved. Note that methyl migration to the metal has occurred in this reaction, as is the case here. Perutz and co-workers have reported in their study of C–H activation with rhodium phosphine and phosphite complexes CpRh(PR_3)(C_2H_4) (R = Me, OMe), in neat arenes under photochemical conditions, that with P($OMe)_3$ a rhodium phosphonate complex was the major product, and the activation of the arene solvent was minor.[22] Other metal–phosphite complexes have been converted to the metal phosphonates by thermolysis.[23]

During the irradiation of **1** in benzene, the benzene activation product Cp*Re(CO){P($OEt)_3$}(Ph)H (**7**) was observed to decay while the intramolecular activation product Cp*Re(CO){η^2-P(OCH_2CH_2)($OEt)_2$}H (**6**) increased. The final products of this reaction were ***cis*-6** and ***trans*-6**. To account for this observation, the intermolecular product **7** must reductively eliminate benzene and the resulting 16-electron intermediate then undergo cyclometalation to produce the intramolecular product (Scheme 1). This means that the intramolecular product is the thermodynamically preferred one, but the intermolecular product is kinetically favored. Furthermore, no *thermal* activation of benzene is observed with these complexes. This result is opposite to that of the previous work with the trimethylphosphine complex, where the cyclometalated complex Cp*Re(L){η^2-PCH_2-($Me)_2$}H (L = CO, PMe_3) converted in benzene to the intermolecular product Cp*Re(L)(PMe_3)(Ph)H.[1,2,16]

A competition between intra- and intermolecular C–H activation was observed by Jones and Feher in the photochemical reaction of Cp*Rh{P(*n*-Pr)Me_2}(H)$_2$ in propane.[24] They proposed that the cyclometalated product was thermodynamically favored but kinetically disfavored. A similar result was observed by Bergman et al. in the photolysis of Cp*Ir(PPh_3)H_2 in benzene, where both inter- and intramolecular C–H products were observed.[7,25] To make the cyclometalation product less favored, the PPh_3 ligand was replaced with PMe_3, whereupon only the intermolecular C–H activation product Cp*Ir(PMe_3)(Ph)H was obtained. This result is in keeping with the notion that crowded conditions arising from ligands with a large cone angle[26] facilitate intramolecular activation.[27]

It is interesting to note the favored direction of the isomerism in the four-legged piano stool cyclometalated complexes **6**, **8**, and **11**. In each case, the cis(P,H) complex is thermodynamically favored over the trans. In terms of the C–H activation involved, it might be anticipated that the agostic complex itself transforms to the trans(P,H) complex, since this is the one in which the carbon and hydride fragments from the agostic C–H bond remain mutually adjacent in a cis arrangement. If this is the case, there must be subsequent isomerization of this stereochemistry to the one with the carbon and hydride fragments mutually trans (i.e., the cis(P,H) complex).[28] Previously, the intermolecular benzene C–H activation complex Cp*Re(CO)(PMe_3)-(Ph)H formed in this piano stool rhenium system was observed only as the isomer with the C and H fragments trans to each other.[1,2,16] Here, however, we have observed that the alternative cis(C,H) isomer (i.e., ***trans(P,H)*-7**) can be produced in the case of **7**.

Conclusion

The UV photolysis of a series of rhenium dinitrogen phosphite and phosphine complexes has been studied in an effort to evaluate the dependence of the reaction products on the nature of the phosphorus ligand. Evidence has been presented supporting the observation of relatively persistent intramolecular agostic intermediates that convert to isomers of cyclometalated phosphite or phosphine C–H activation complexes as the ultimate products. This chemistry competes with intermolecular activation of an aromatic hydrocarbon such as benzene. However, for the trimethyl phosphite complex this was not observed; instead, there was migration of a methyl group to rhenium to afford a methylrhenium phosphonate complex.

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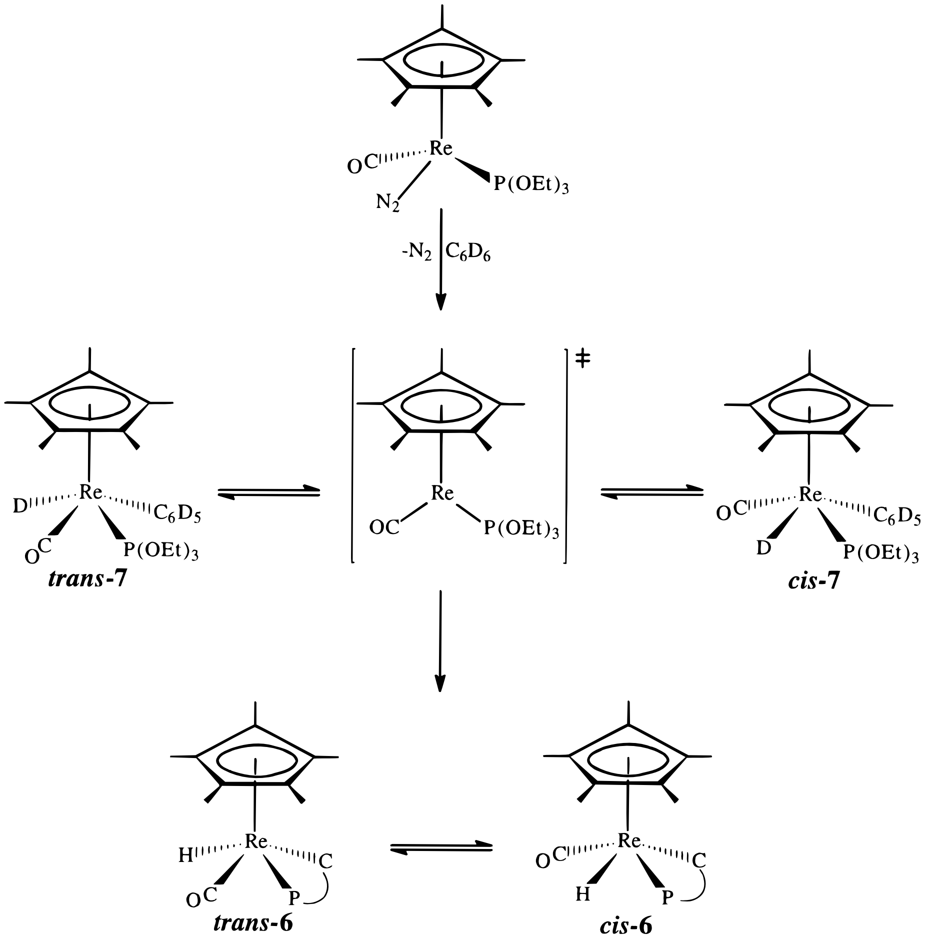
Scheme 1. Proposed Scheme for the Formation of Intermolecular and Intramolecular Products from the Photolysis of 1 in Benzene



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 273−277 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. Hexane, benzene, and cyclohexane were distilled over Na using standard methods and were transferred directly into the Pyrex reaction tube under nitrogen.

All the NMR data were recorded on a Bruker AMX 400 instrument at operating frequencies of 400, 162, and 100 MHz for ^{1}H, ^{31}P, and ^{13}C nuclei, respectively. The ^{1}H and ^{13}C{^{1}H} NMR chemical shifts are reported in ppm downfield (positive) of tetramethylsilane. The ^{1}H NMR spectra in nondeuterated solvents were recorded using a standard suppression program from the Bruker pulse program library. The ^{31}P NMR chemical shifts are referenced to an external 85% H_3PO_4 sample. The deuterated solvents used for NMR spectroscopy were degassed prior to use to remove any residual oxygen.

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 ^{187}Re isotope. Microanalyses were performed by the Simon Fraser University Microanalytical Laboratory.

Syntheses. Details of the preparation and characterization of Cp*Re(CO)(L)(N_2) (L = P(OMe)$_3$, Pc, PPh$_3$) (**3**−**5**) have been given previously.[29] The following were synthesized similarly. Data for **Cp*Re(CO){P(OEt)$_3$}(N$_2$)** (**1**): IR (hexane) ν_{N_2} 2060, ν_{CO} 1875 cm^{-1}; ^{1}H NMR (acetone-*d*$_6$) δ 1.23 (t, 9H, P(OCH$_2$C*H*$_3$)$_3$, J_{HH} = 7.0 Hz), 1.95 (s, 15H, C$_5$Me$_5$), 3.81 (m, 6H, P(OC*H*$_2$-CH$_3$)$_3$); ^{31}P{^{1}H} NMR (CDCl$_3$) δ 129.49; MS (EI) *m*/*z* 544 (M$^+$), 516 (M$^+$ − N$_2$). Anal. Calcd for $C_{17}H_{30}N_2O_4PRe$: C, 37.56; H, 5.56; N, 5.15. Found: C, 37.17; H, 5.13; N, 5.12. Data for **Cp*Re(CO){P(OPh)$_3$}(N$_2$)** (**2**): IR (hexane) ν_{N_2} 2095, ν_{CO} 1898 cm^{-1}; ^{1}H NMR (acetone-*d*$_6$) δ 1.64 (s, 15H, C$_5$Me$_5$), 7.15−7.45 (m, 15H, P(OC$_6$H$_5$)). MS (EI) *m*/*z* 688 (M$^+$), 660 (M$^+$ − N$_2$). Anal. Calcd for $C_{29}H_{30}N_2O_4PRe$: C, 50.65; H, 4.40; N, 4.07. Found: C, 50.55; H, 4.32; N, 4.03.

Photolysis of Cp*Re(CO){P(OEt)$_3$}(N$_2$) (1) in Hexane. A solution of **1** (20 mg, 0.036 mmol) in hexane (8 mL) was irradiated for 10 min at 278 K. The IR spectrum of the solution showed the complete disappearance of **1**. The solvent was removed under vacuum at 273 K, and the residue was dissolved in toluene-*d*$_8$ without purification. The ^{1}H NMR spectrum of this solution showed complexes ***agostic*-6**, ***trans-(P,H)*-6**, and ***cis(P,H)*-6** to be present in a ratio of 66:26:7 from integration of the hydride resonances. Data for ***agostic*-6**: IR (hexane) 1860 cm^{-1} ν_{CO}; ^{1}H NMR (toluene-*d*$_8$) at 273 K δ −9.82 (d, 1H, Re−H, J_{PH} = 12.0 Hz), 1.08 (t, *J* = 7.0 Hz, P(O-CH$_2$C*H*$_3$)$_2$), 1.25 (t, *J* = 7.0 Hz, P(OCH$_2$C*H*$_3$)$_2$), 1.49 (m, POCH$_2$C*H*$_2$), 1.87 (s, J_{PH} = 0.6 Hz, C$_5$Me$_5$) 2.85 (m, 1H, P(OCH$_2$C*H*$_2$), 3.32 (m, POC*H*$_2$CH$_2$), 4.05 (m, 1H, POC*H*$_2$CH$_2$), 3.70−4.30 (m, P(OC*H*$_2$CH$_3$)$_2$); ^{31}P NMR (benzene-*d*$_6$) at 293 K δ 163.93 (s). Data for ***trans(P,H)*-6**: IR (hexane) 1898 cm^{-1}

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ν_{CO}; ^{1}H NMR (toluene-d_8) at 293 K δ −10.11 (d, 1H, Re−H, J_{PH} = 28.0 Hz), 1.86 (s, C$_5$Me$_5$), 1.23 (t, 3H, J = 7.0 Hz, P(OCH$_2$CH_3)$_2$), 1.27 (t, 3H, J = 7.0 Hz, P(OCH$_2$CH_3)$_2$); ^{31}P NMR (benzene-d_6) δ 46.62 (d, J_{PH} = 27.0 Hz). Data for ***cis-(P,H)*-6**: IR (hexane) 1898 cm^{-1} ν_{CO}; ^{1}H NMR (toluene-d_8) at 293 K δ −10.20 (d, 1H, Re−H, J_{PH} = 60.0 Hz), 1.85 (d, J_{PH} = 0.8 Hz, C$_5$Me$_5$), 1.08 (t, 3H, J = 7.0 Hz, P(OCH$_2$CH_3)$_2$), 1.13 (t, 3H, J = 7.0 Hz, P(OCH$_2$CH_3)$_2$), 2.39 (m, 1H, J = 5.6 Hz, J = 2.0 Hz, POCH$_2$CH$_2$), 3.40 (m, 2H, J = 6.5 Hz, POCH$_2$CH$_2$); ^{31}P NMR (benzene-d_6) δ 158.89 (d, J_{PH} = 58.8 Hz). The ethoxy methylene protons for the cyclometalated products (***trans-(P,H)*-6** and ***cis(P,H)*-6)** in the ^{1}H NMR were overlapped in the range 3.75−4.40 ppm. Attempted separation and purification of the complexes by either solvent extraction or column chromatography failed to produce pure products.

Photolysis of Cp*Re(CO){P(OEt)$_3$}(N$_2$) (1) in Benzene-*d*$_6$. A solution of **1** (10 mg, 0.018 mmol) in benzene-d_6 (3 mL) was irradiated for 12 min. The IR spectrum of the solution showed the complete disappearance of **1**. Immediately after irradiation, an ^{1}H NMR spectrum was taken without purification. This showed the presence of ***cis*-6, *trans*-6**, ***cis*-7, *trans*-7**, and ***agostic*-6**. IR (benzene-d_6): 1885 cm^{-1} (broad) ν_{CO}. ^{1}H NMR (benzene-d_6): for ***cis(P,H)*-6**, δ −10.28 (d, Re−H, J_{PH} = 60.0 Hz), 1.11 (t, P(OCH$_2$CH_3)$_2$, J = 7.0 Hz), 1.18 (t, P(OCH$_2$CH_3)$_2$, J = 7.0 Hz), 1.88 (s, C$_5$Me$_5$); for ***trans(P,H)*-6**, δ −9.98 (d, 1H, Re−H, J_{PH} = 28.0 Hz), 1.25 (t, P(OCH$_2$CH_3)$_2$, J = 7.0 Hz), 1.32 (t, P(OCH$_2$CH_3)$_2$, J = 7.0 Hz), 1.89 (s, C$_5$Me$_5$); for ***cis(P,H)*-7**, δ 1.02 (t, P(OCH$_2$CH_3)$_3$, J = 7.0 Hz), 1.10 (t, P(OCH$_2$CH_3)$_3$, J = 7.0 Hz), 1.83 (s, C$_5$Me$_5$) 3.74 (m, P(OCH_2CH$_3$)$_3$), 3.95 (m, P(OCH_2CH$_3$)$_3$); for ***trans(P,H)*-7**, δ 1.86 (s, C$_5$Me$_5$). The resonances for the ethoxy group methyls in ***trans(P,H)*-7** and methylenes in **6** and ***trans(P,H)*-7** appeared in the ranges 1.15−1.35 and 3.70−4.40 ppm, respectively. The sample was monitored by ^{1}H and ^{31}P NMR in benzene-d_6 at room temperature, and the results have been given under Results. Separation and purification of the metal hydride complexes by either solvent extraction or column chromatography failed to produce pure products.

Photolysis of Cp*Re(CO){P(OPh)$_3$}(N$_2$) (2) in Hexane, Benzene, or Cyclohexane. A solution of **2** (50 mg, 0.07 mmol) in 10 mL of freshly distilled benzene was twice freeze−pump−thaw degassed and then irradiated for 9 min at 277 K. The IR spectrum after the photolysis reaction indicated the disappearance of **2**. The solvent was removed, the residual solid was redissolved in ca. 2 mL of benzene, and the solution was transferred to an air-free neutral alumina column and eluted with a mixture of benzene−hexane (2:1). Evaporation of the solvent under vacuum gave ***cis(P,H)*-8** as a pale yellow solid, which was recrystallized from benzene−hexane at 258 K in 80% yield (38 mg, 0.058 mmol). IR (hexane): 1946 cm^{-1} ν_{CO}. ^{1}H NMR (acetone-d_6): δ −10.09 (d, 1H, ReH, J_{PH} = 63 Hz), 2.03 (s, 15H, C$_5$Me$_5$), 6.79−7.46 (m, 14H, η^2-P(OC$_6$$H_4$)(OC$_6$$H_5$)$_2$). ^{13}C{^{1}H}NMR (benzene-d_6): δ 10.94 (s, C$_5$$Me_5$), 97.55 (s, C_5Me$_5$), 110.14 (d, η^2-P(OC_6H$_4$)(OC_6H$_5$)$_2$, J_{CP} = 15.2 Hz), 121.42 (d, η^2-P(OC_6H$_4$)(OC_6H$_5$)$_2$, J_{CP} = 4.6 Hz), 121.70 (d, η^2-P(OC_6H$_4$)(OC_6H$_5$)$_2$, J_{CP} = 4.6 Hz), 123.32 (s, η^2-P(OC_6H$_4$)(OC_6H$_5$)$_2$), 124.00 (s, η^2-P(OC_6H$_4$)(OC_6H$_5$)$_2$), 125.22 (s, η^2-P(OC_6H$_4$)(OC_6H$_5$)$_2$), 126.86 (s, η^2-P(OC_6H$_4$)(OC_6H$_5$)$_2$), 129.78 (d, η^2-P(OC_6H$_4$)(OC_6H$_5$)$_2$, J_{CP} = 9.2 Hz), 132.52 (d, η^2-P(OC_6H$_4$)(OC_6H$_5$)$_2$, J_{CP} = 16.0 Hz), 144.29 (d, η^2-P(OC_6H$_4$)(OC_6H$_5$)$_2$, J_{CP} = 5.3 Hz), 152.01 (d, η^2-P(OC_6H$_4$)(OC_6H$_5$)$_2$, J_{CP} = 3.8 Hz), 153.39 (d, η^2-P(OC_6H$_4$)(OC_6H$_5$)$_2$, J_{CP} = 16.0 Hz), 162.99 (d, η^2-P(OC_6H$_4$)(OC_6H$_5$)$_2$, J_{CP} = 25.9 Hz), 202.38 (d, CO, J_{CP} = 15 Hz). ^{31}P{^{1}H} (acetone-d_6): δ 83.49 (s). MS (EI): m/z 660 (M$^+$), 630 (M$^+$ − CO − 2H), 537 (M$^+$ − CO − 2H − OC$_6$H$_4$). Anal. Calcd for C$_{29}$H$_{30}$O$_4$PRe: C, 52.80; H, 4.58. Found: C, 52.69; H, 4.60.

Photolysis of 2 in Benzene-*d*$_6$. A solution of **2** (10 mg, 0 0.015 mmol) in benzene-d_6 (2 mL) was irradiated for 5 min. Immediately after the irradiation and without purification, an ^{1}H NMR spectrum was taken. The ^{1}H NMR spectrum showed ***cis*-8** to be present as a minor product. The spectrum also exhibited a broad doublet (δ −7.95, J_{PH} = 11.0 Hz) assigned to ***agostic*-8**. IR (benzene-d_6): 1933 cm^{-1} ν_{CO}. ^{1}H NMR (benzene-d_6) (***cis*-8:*agostic*-8** = 36:64): δ −9.78 (d, ReH, J_{PH} = 62.9 Hz), −7.95 (d, ReH, J_{PH} = 11.0 Hz), 1.84 (s, C$_5$Me$_5$), 2.03 (s, C$_5$Me$_5$), 6.79−7.46 (m, η^2-P(OC$_6$$H_4$)(OC$_6$$H_5$)$_2$). The ^{1}H NMR spectrum of the same sample acquired after 3 h showed the total disappearance of ***agostic*-8** and the concomitant growth of ***cis*-8**. Conversion from ***agostic*-8** to ***cis*-8** was estimated to be ca. 95% complete by ^{1}H NMR.

Photolysis of Cp*Re(CO)(Pc)(N$_2$) (3) in Hexane. A solution of dinitrogen complex **3** (12 mg, 0.022 mmol) in hexane (5 mL) was irradiated for 10 min. An IR spectrum of the resulting green solution showed the total disappearance of **3** and no evidence of any product. Immediately after the irradiation, the solvent was removed under vacuum at room temperature and the residue was taken up in benzene-d_6 without purification. The ^{1}H NMR spectrum of this solution exhibited only resonances for some of the free Pc ligand and organic materials that were not identified.

Photolysis of 3 in Benzene. A solution of **3** (20 mg, 0.038 mmol) in benzene (6 mL) was irradiated for 10 min. The IR spectrum of the slightly yellow solution indicated the total disappearance of **3**. The sample was taken up in benzene without purification. An ^{1}H NMR spectrum of this solution exhibited one resonance in the metal hydride region. IR (benzene): 1913 cm^{-1} ν_{CO}. ^{1}H NMR (benzene): δ −9.20 (d, 1H, Re−H, J_{PH} = 68.8 Hz), −0.50 (s, 3H, P(OCH$_2$)$_3$CCH_3), 1.72 (s, 15H, C$_5$Me$_5$), 3.34 (d, 6H, P(OCH_2)$_3$CCH$_3$, J_{PH} = 6.0 Hz). From the limited spectroscopic evidence, this was assigned as the intermolecular benzene C−H activation product *cis*-Cp*Re(CO)(Pc)(C$_6$H$_5$)H **(*cis*-9)**. An ^{1}H NMR spectrum of the same sample acquired after 1 h at room temperature showed a decrease in intensity in the metal hydride region. Purification of the new complex by either solvent extraction or column chromatography failed.

Photolysis of Cp*Re(CO){P(OMe)$_3$}(N$_2$) (4) in Hexane, Cyclohexane, or Benzene. A solution of **4** (50 mg, 0.10 mmol) in hexane (10 mL) was irradiated for 15 min. An IR spectrum of the resulting brown-yellow solution showed the total disappearance of **4**. After removal of the volatile materials under vacuum at room temperature, the residue was redissolved in ca. 2 mL of hexane, and the solution was carefully transferred to an air-free neutral alumina column and eluted with hexanes−ether (4:1). Removal of the solvent under vacuum gave a yellow solid, which was recrystallized from hexane at 265 K to provide **10** as a pale yellow solid in 49% yield (23 mg, 0.024 mmol). IR (hexane): 1900, 1879 cm^{-1} ν_{CO}. ^{1}H NMR (acetone-d_6): δ 0.74 (s, 3H, Re−CH$_3$), 1.68 (s, 15H, C$_5$Me$_5$), 3.42 (d, 3H, PO(OMe)$_2$, J_{PH} = 8.0 Hz), 3.49 (d, 3H, PO(OMe)$_2$, J_{PH} = 8.0 Hz). ^{13}C{^{1}H}NMR (acetone-d_6): δ −0.98 (d, J_{CP} = 11.7 Hz, Re−CH$_3$), 10.15 (s, C$_5$Me$_5$), 51.35 (d, PO(OCH$_3$)$_2$, J_{CP} = 11.4 Hz), 52.66 (d, PO(OCH$_3$)$_2$, J_{CP} = 11.4 Hz), 100.42 (s, C_5Me$_5$), 221.35 (d, CO, J_{CP} = 28.9 Hz). ^{31}P{^{1}H} (acetone-d_6): δ 80.70 (s). MS (EI): m/z 946 (M$^+$), 918 (M$^+$ − CO), 844 (M$^+$ − CO − C$_4$H$_{10}$O). Anal. Calcd for C$_{28}$H$_{48}$O$_8$P$_2$Re$_2$: C, 35.52; H, 5.07. Found: C, 35.55; H, 4.98.

Photolysis of Cp*Re(CO)(PPh$_3$)(N$_2$) (5) in Benzene, Benzene-*d*$_6$, Hexane, or Cyclohexane. A solution of **5** (50 mg, 0.07 mmol) in 10 mL of freshly distilled benzene was twice freeze−pump−thaw degassed and then irradiated for 10 min at 277 K. The IR spectrum after the photolysis indicated the disappearance of **5**. Immediately after the irradiation and without purification, an ^{1}H NMR spectrum was taken, which showed the presence of ***cis*-11** and a broad doublet in the metal hydride region assigned to ***agostic*-11.** IR (benzene): 1913 cm^{-1} ν_{CO}. ^{1}H NMR (benzene): ***agostic*-11** δ −7.55 (d, ReH, J_{PH} = 12 Hz), 1.69 (s, C$_5$Me$_5$); ***cis*-11** δ −7.89 (d, ReH, J_{PH} = 73 Hz), 1.78 (s, C$_5$Me$_5$).

Reaction of *cis*-Cp*Re(CO){η^2-P(C_6H_4)Ph_2}(H) (*cis*-11) with $CHCl_3$ or $CDCl_3$. The intramolecular C−H activation product ***cis*-11** was dissolved in $CHCl_3$ or $CDCl_3$ (2 mL) at room temperature under nitrogen and the solution stirred for 3 h. An ^{1}H NMR spectrum ($CDCl_3$) of the solution showed the complete disappearance of ***cis*-11** and the presence of *cis*-Cp*Re(CO){η^2-P(C_6H_4)Ph_2}Cl **(*cis*-12)**. Removal of the solvent under vacuum and subsequent extraction with diethyl ether (3 × 20 mL) gave ***cis*-12** as a yellow-orange solid. IR (benzene): 1908 cm^{-1} ν_{CO}. ^{1}H NMR ($CDCl_3$): δ 1.53 (s, 15H, C_5Me_5), 6.92 (m, 2H, η^2-P(C_6H_4)Ph_2), 7.14 (m, 1H, η^2-P(C_6H_4)-Ph_2, 7.25 (m, 1H, η^2-P(C_6H_4)Ph_2), 7.31 (m, 3H, η^2-P(C_6H_4)Ph_2), 7.46 (m, 3H, η^2-P(C_6H_4)Ph_2), 7.55 (m, 2H, η^2-P(C_6H_4)Ph_2), 7.76 (m, 2H, η^2-P(C_6H_4)Ph_2). ^{13}C{^{1}H}NMR ($CDCl_3$): δ 9.62 (s, $C_5\mathit{Me}_5$), 101.02 (s, C_5Me_5), 123.50−137.51 (η^2-P(C_6H_4)(C_6H_5)$_2$), 209.64 (s, *C*O). MS (EI): *m*/*z* 646 (M^+), 618 (M^+ − CO). Anal. Calcd for $C_{29}H_{29}ClOPRe$: C, 53.91; H, 4.49. Found: C, 53.73; H, 4.59.

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