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A comparison of trimethylphosphine and tricyclohexylphosphine complexes $(\eta^5\text{-}C_5Me_5)Re(CO)(PR_3)(N_2)$ (R = Me, cyclo-C_6H_{11}) in inter- and intra-molecular C–H activation reactions. X-ray structure of the cyclometallated product $(\eta^5\text{-}C_5Me_5)Re(\eta^2\text{-}C_6H_{10}P\{C_6H_{11}\}_2)(H)(CO) \cdot 0.5C_6H_{14}$

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Abstract

Irradiation of $(\eta^5\text{-}C_5Me_5)Re(CO)(PMe_3)(N_2)$ (**1**) in benzene forms *trans*-(H,Ph)-$(\eta^5\text{-}C_5Me_5)Re(CO)(PMe_3)(H)(Ph)$ (**4**), whereas irradiation in cyclohexane results in intramolecular C–H activation of the PMe_3 group, yielding *trans*-(H,CH_2)-$(\eta^5\text{-}C_5Me_5)Re(\eta^2\text{-}CH_2PMe_2)(CO)(H)$ (**5**). By contrast, irradiation of $(\eta^5\text{-}C_5Me_5)Re(CO)(P\{C_6H_{11}\}_3)(N_2)$ (**2**) in benzene does not result in any observable product derived from intermolecular C–H activation of benzene. Instead, intramolecular C–H activation of the tricyclohexylphosphine ligand occurs, as it does when **2** is irradiated in cyclohexane, to give the C-1 (*ipso*) cyclometallated product $(\eta^5\text{-}C_5Me_5)Re(\eta^2\text{-}C_6H_{10}P\{C_6H_{11}\}_2)(H)(CO)$ (**3**). The crystal structure of **3** has been determined at 212 K. Distances and angles in the 3-membered metallacycle are Re(1)–P(1) 2.324(6), Re(1)–C(21) 2.27(2), P(1)–C(21) 1.77(3) Å, C(21)–Re(1)–P(1) 45.2(8), C(21)–P(1)–Re(1) 65.9(7), P(1)–C(21)–Re(1) 68.9(7)°. Other pertinent dimensions are Re–C(1) 1.75(2), C(1)–O(1) 1.26(2), P(1)–C(31) 1.84(2), P(1)–C(41) 1.86(2) Å, Re(1)–C(1)–O(1) 1.76(2), C(31)–P(1)–Re(1) 117.4(7), C(31)–P(1)–C(21) 114.2(10), C(41)–P(1)–Re(1) 126.2(7), C(21)–P(1)–C(41) 114.1(9) and C(31)–P(1)–C(41) 110.8(10)°. The hydride ligand was not located but it is reasoned to be in a position pseudo-*trans* to the phosphorus atom in a four-legged piano stool structure; there was no observable $^2J(HP)$ coupling for the hydride resonance in the ^1H NMR spectrum.

Introduction

Some time ago, we communicated briefly [1] results that showed the dinitrogen complex [2] $Cp^{\star}Re(CO)(PMe_3)(N_2)$ (**1**) ($Cp^{\star} = \eta^5\text{-}C_5Me_5$) to be a very convenient alternative to rhenium trimethylphosphine carbonyl complexes [3] in promoting C–H activation of benzene. This is because of the rather short (ca. 5–10 min) irradiation time required for virtually quantitative reaction, reflecting much easier photochemical loss of N_2 compared with CO or PMe_3. With the availability of a series of these phosphine complexes $Cp^{\star}Re(CO)(PR_3)(N_2)$ at hand [2] we now have investigated the corresponding tricyclohexylphosphine complex $Cp^{\star}Re(CO)(P\{C_6H_{11}\}_3)(N_2)$ (**2**). This was chosen since from the lower relative positions of ν(NN) and ν(CO) rhenium in the latter may be rather more electron-rich, and this might be a possible factor in promoting C–H activation in these systems [4]. On the other hand, the cone angles [5] of these trialkylphosphine ligands ($PMe_3 = 118°$; $P\{C_6H_{11}\}_3 = 170°$) indicate them to differ considerably in steric bulk, which is another factor to be considered. Here we provide a detailed comparison of the photolysis of **2** and **3** in benzene and cyclohexane. We find that the intermolecular C–H activation of benzene is completely suppressed when **1** is replaced by **2**. Instead, intramolecular C–H activation of one cyclohexyl group occurs at the *ipso* position resulting in the complex $Cp^{\star}Re(\eta^2\text{-}C_6H_{10}P\{C_6H_{11}\}_2)(H)(CO)$ (**3**) which has been characterized crystallographically. Irradiation of **1** and **2** in cyclohexane results in the cyclometallated products $Cp^{\star}Re(\eta^2\text{-}CH_2PMe_2)(H)(CO)$ (**5**) and **3** respectively. These have different stereochemistries: in **3** H is *trans* to P, but in **5** H and P are *cis*.

Experimental

(a) General methods

Manipulations were performed under oxygen-free nitrogen by the use of Schlenk tubes, dry box or vacuum line techniques. Infrared spectra were measured using a Perkin Elmer model 938G instrument and 0.1 mm CaF_2 cells with the appropriate solvent in the reference cell. ^1H NMR spectra were recorded on a Bruker WM-400 instrument at 400 MHz or on a Bruker SY-100 instrument at 100 MHz. Mass spectra were obtained on a Hewlett-Packard Model 5985 spectrometer by Mr. G. Owen and masses are quoted for the ^{187}Re isotope. Elemental analyses were performed by Mr. M.K. Yang of the S.F.U. Microanalytical Laboratory.

Benzene was distilled from dark purple solutions of sodium benzophenone ketyl under a nitrogen atmosphere. Pentane, hexane, and cyclohexane were distilled over sodium wire under nitrogen. Decacarbonyldirhenium, trimethylphosphine, and tricyclohexylphosphine were purchased from the Strem Chemical Co.; all were used without further purification.

All photochemical reactions were carried out under oxygen-free nitrogen with the use of a 200 W Hanovia high-pressure mercury lamp; solutions were in 10 ml or 20 ml quartz or Pyrex photolysis tubes placed beside the lamp. $Cp^{\star}Re(CO)(PR_3)(N_2)$ ($PR_3 = PMe_3$ (**1**), $Pcy_3\{cy = cyclo\text{-}C_6H_{11}\}$ (**2**)) were synthesized as described previously [2].

Irradiation of $(\eta^5\text{-}C_5Me_5)Re(CO)(PMe_3)(N_2)$ (1).

(a) in benzene. A solution of $Cp^{\star}Re(CO)(PMe_3)(N_2)$ (**1**) (100 mg, 0.220 mmol) in about 15 ml of freshly distilled benzene was degassed by two freeze-pump-thaw cycles and then irradiated for 10 min at 10 °C. During the photolysis a slow flux of N_2 was maintained. The IR spectrum of the slightly yellow solution indicated a

quantitative conversion of **1** into a monocarbonyl containing compound. After removal of the solvent under vacuum at room temperature, the residual oily solid was redissolved in about 2 ml of benzene and carefully 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 *trans*-(H,Ph)-Cp*Re(CO)(PMe$_3$)(H)(Ph) (**4**) as a white solid which was recrystallized from freshly distilled hexane at −78 °C. M.p. slow decomposition above 75 °C. IR (C_6H_6): 1872s, ν(CO), cm^{-1} (1899 cm^{-1} in hexane). ^{1}H NMR (C_6D_6): δ −9.18 d (^2J(PH) 66.7, 1H, Re–H), 1.08 d (^2J(PH) 8.9, 9H, PMe$_3$), 1.81 s (15H, Cp*), 7.16 m (3H, *m*-Ph and *p*-Ph), 7.96 m (2H, *o*-Ph). ^{13}C NMR (C_6D_6): δ 11.47 q (J(CH) 127.0, C$_5$*Me*$_5$), 22.56 q of d (^1J(CH) 128.9, ^2J(CP) 34.9, PMe$_3$), 95.97 s (*C*$_5$Me$_5$), 123.34 d (^1J(CH) 157.2, *p*-Ph), 126.94 d (^1J(CH) 154.0, *m*-Ph), 144.87 d (^2J(CP) 23.3, *i*-Ph), 147.31 d of d (^1J(CH) 150.7, ^3J(CP) 5.41, *o*-Ph), 209.02 d (^2J(CH) 10.8 {singlet in ^{13}C{^{1}H} NMR} CO). MS (EI, 12 eV): *m/z* 504 (M^+), 426 ($M - C_6H_6$)$^+$ base peak. Anal. Found: C, 47.88; H, 6.20. $C_{20}H_{30}OPRe$ calcd.: C, 47.62; H, 5.95%.

(b) in hexane or cyclohexane. Cp*Re(CO)(PMe$_3$)(N$_2$) (**1**) (20 mg, 0.044 mmol) was dissolved in about 10 ml of freshly distilled hexane or cyclohexane and degassed twice. This solution was then irradiated for 8 min through a quartz tube with N$_2$ purge. The IR spectrum of the resulting light-brown solution showed only the presence of **5**. Evaporation of the solvent under vacuum gave a brown solid which was redissolved in about 3 ml of hexane and filtered through a short neutral alumina column and stored at −78 °C for two or three days. The white microcrystalline solid was isolated by decanting the supernatant solution and drying under vacuum at −78 °C for 3 h. Estimated yield 60% based on **1**. M.p. decomposed above 50 °C. IR (cyclohexane): 1878s, ν(CO), cm^{-1}. ^{1}H NMR (cyclohexane-d_{12}): δ −9.92 d (^2J(PH) 38.2, 1H, Re–H), −0.57 d of d (^2J(HH) 7.3, ^2J(PH) 3.0, 1H, H$_b$), 0.57 d of d (^2J(HH) 7.3, ^2J(PH) 4.3, 1H, H$_a$), 1.37 d (^2J(PH) 11.8, 3H, Me$_b$), 1.55 d (^2J(PH) 12.9, 3H, Me$_a$), 2.02 s (15H, Cp*). MS (EI, 12 eV): *m/z* 426 (M^+) (at 70 eV only a spectrum with prominent peaks at *m/z* 502, 474 and 426 was observed).

Irradiation of (η^5-C$_5$Me$_5$)Re(CO)(Pcy$_3$)(N$_2$) (2)

(a) in benzene. Cp*Re(CO)(Pcy$_3$)(N$_2$) (**2**) (54.0 mg, 0.0821 mmol) was dissolved in 7.5 ml of freshly distilled benzene in a 20 ml quartz tube and the solution was degassed with two freeze-pump-thaw cycles (IR (benzene): 2023s, ν(NN), 1842vs, ν(CO), cm^{-1}). After 15 min of irradiation at 0 °C with a constant flux of nitrogen the IR spectrum of the resulting brown solution showed the complete disappearance of the starting material and a single carbonyl absorption at 1836 cm^{-1}. The volume of benzene was reduced to ca. 1 ml and the solution was chromatographed on a short column of deactivated neutral alumina. The remainder of the solvent was then removed by vacuum and the product was recrystallized from ca. 1 ml of hexane at −78 °C. The off-white crystals obtained were washed several times with ice-cold hexane to remove any unreacted starting material present. The product was isolated and pumped to dryness by vacuum for ca. 1.5 h. The reaction was repeated on smaller scales to compare results using quartz and Pyrex photolysis tubes and gave the same product by IR and ^{1}H NMR spectroscopy. Yield: 31.2 mg (60.0%). IR (benzene): 1836 cm^{-1} ν(CO). IR (hexane): 1852 cm^{-1} ν(CO). ^{1}H NMR (100 MHz; C_6D_6): δ −8.64 s (1H, Re–H), 1.16–1.51, 1.61–1.93 m (32H, η^2-Pcy$_2$C$_6$H$_{10}$), 2.07 s (15H, C$_5$Me$_5$). ^{1}H NMR (100 MHz; (CD$_3$)$_2$CO): δ −9.2 s (1H, Re–H), 1.36, 1.60,

1.68–1.94 m (32H, η^2-$Pcy_2C_6H_{10}$), 1.96 s (15H, C_5Me_5). MS (EI; 12 eV): *m/z* 630 (M^+), 548 ($M^+ - C_6H_{10}$), 466 ($M^+ - 2C_6H_{10}$). Anal. Found: C., 57.14; H, 8.40. $C_{32}H_{55}OPRe$ calcd.: C, 57.11; H, 8.24%.

(b) in benzene-d_6. $Cp^\star Re(CO)(Pcy_3)(N_2)$ (**2**) (5.0 mg, 0.0076 mmol) was dissolved in 1.0 ml of benzene-d_6 in a sealed Pyrex NMR tube under nitrogen. The solution was irradiated for 10 min at 0 °C. The IR spectrum of the resulting brown solution showed the complete disappearance of the dinitrogen complex and a single carbonyl absorption at 1834 cm^{-1}. The ^1H NMR spectrum of this solution again showed only a single hydride product. IR (C_6D_6): 1834 $\nu(CO)$ cm^{-1}. ^1H NMR (C_6D_6): δ −8.66 s (1H, Re–H), 1.11–1.42, 1.65–1.91 m (32H, η^2-$Pcy_2C_6H_{10}$), 2.06 s (15H, C_5Me_5).

(c) in cyclohexane. $Cp^\star Re(CO)(Pcy_3)(N_2)$ (**2**) (13.0 mg, 0.020 mmol) was dissolved in 3 ml of freshly distilled cyclohexane in a 20 ml quartz tube and the solution was degassed by two freeze-pump-thaw cycles. (IR (cyclohexane): 2030s, $\nu(NN)$, 1855vs, $\nu(CO)$ cm^{-1}). After 15 min of irradiation at 0 °C with a constant flux of nitrogen the IR spectrum of the resulting brown solution showed the complete disappearance of the starting material and a single carbonyl absorption at 1850 cm^{-1}. The solvent was removed by vacuum and the resulting brown oily solid was dissolved in 0.5 ml of C_6D_6 and the ^1H NMR spectrum was obtained. Again, a single hydride resonance appeared in the NMR spectrum at δ −8.66. The experiment was repeated again on the same scale and this time a ^1H NMR spectrum was obtained in acetone-d_6 solution. The hydride resonance occurred at δ −9.1, but now no phenyl hydrogen resonances were observed confirming that a resonance at δ 7.21 ppm in the previous spectrum run in benzene-d_6 was solely due to residual protons in the deuterated solvent. IR (cyclohexane): 1850, $\nu(CO)$ cm^{-1}. ^1H NMR (100 MHz; C_6D_6): δ −8.64 s (1H, Re–H), 1.18–1.31, 1.61–1.92 m (32H, η^2-$Pcy_2C_6H_{10}$), 2.07 s (15H, C_5Me_5). ^1H NMR (100 MHz; $(CD_3)_2CO$): δ −9.1 s (1H, Re–H), 1.25, 1.60–1.91 m, (32H, η^2-$Pcy_2C_6H_{10}$), 2.08 s (15H, C_5Me_5).

High pressure reactions under nitrogen

(a) $Cp^\star Re(\eta^2$-$CH_2PMe_2)(CO)(H)$ (5). Compound **5** (10 mg, 0.019 mmol) was dissolved in freshly distilled hexane (ca. 8 ml) at 0 °C under nitrogen. This solution was carefully transferred to a Parr bomb under nitrogen and pressurized to 2000 psi with oxygen-free nitrogen for 5 h at room temperature. After this time, complete generation of the dinitrogen complex **1** was observed by IR. Evaporation of the solvent gave 9 mg (~ 95% yield) of the dinitrogen complex **1**.

(b) $Cp^\star Re(CO)(PMe_3)(H)(Ph)$ (4). This reaction was carried out as described in (a). An IR spectrum after 5 h showed the presence of the starting complex and **1** in about 1/1 ratio. Additional 7 h under 2000 psi of N_2 gave almost quantitative conversion. From 10 mg of $Cp^\star Re(CO)(PMe_3)(H)(Ph)$, 7.8 mg (96%) of **1** was isolated.

X-ray structure determination for 3

A suitable crystal of **3** was sealed in a Lindemann capillary and transferred to an Enraf–Nonius CAD4-F diffractometer equipped with graphite monochromated Mo–K_α radiation. The crystal was cooled to 212 K by using a locally developed low-temperature apparatus based on the commercial Enraf–Nonius system. The unit cell was obtained from the accurate setting angles of reflections (15° $< 2\theta <$

Table 1

Crystallographic and experimental data for 3.

Crystal data	
Compound	$Re\{P(C_6H_{10})(C_6H_{11})_2\}(H)(CO)Cp^{\star}\cdot 0.5C_6H_{14}$
Formula	$C_{32}H_{55}OPRe$
Molecular weight	672.97
Crystal system	Monoclinic
Space group	$P2_1/n$
a, Å	10.565(2)
b, Å	20.312(6)
c, Å	14.964(3)
β, °	100.78(2)
V, Å^3	3154.55
Z	4
μ(Mo-K_α), mm^{-1}	3.974
D_{calc}, Mg m^{-3}	1.417
Data collection and refinement	
Crystal dimensions, mm	0.10 × 0.18 × 0.06
Temperature, K	212
Radiation, Å	Mo-K_α 0.71069
Transmission factors	0.590–0.810
Scan mode	Coupled ω–2θ
Scan speed range, ° min^{-1}	0.87–0.97
Scan width, °	$0.85 + 0.35 \tan\theta$
Theta limits, °	$4 < 2\theta \leq 45$
Data collection range	$h, k, \pm l$
Unique reflections	4150
Observed reflections ($I \geq 3\sigma(I)$)	1777
Number of variables	139
R_F [a]	0.063
R_{wF} [b]	0.053
Goodness of fit [c]	1.062

[a] $R_F = \Sigma \| F_o| - |F_c\| / \Sigma |F_o|$. [b] $R_{wF} = [\Sigma w(|F_o| - |F_c|)^2/\Sigma F_o^2]^{1/2}$. [c] Goodness of fit $= [\Sigma w(|F_o| - |F_c|)^2/(\text{No. of degrees of freedom})]^{1/2}$.

23°) from diverse regions of reciprocal space. Three standard reflections, measured every hour, showed a decrease of intensity of 10.5% at one stage during the data collection and also movement of the crystal (the general overall instability of the standard reflections was of the order 2.1%). The data were therefore scaled in two blocks, using a five point smoothing curve within each block. The data were corrected for Lorentz polarization and analytically for absorption effects [6]. Pertinent crystallographic and experimental parameters are given in Table 1.

The structure was solved by heavy atom methods, and refined by full-matrix least-squares. A solvent molecule of hexane was located on the crystallographic centre of symmetry. During the course of the refinement it became apparent that the hexane molecule was disordered such that the carbon atom adjacent to the terminal carbon atom occupied two sites. The two sites were included in the refinement with a variable occupancy (constrained to sum to unity). Restraints were applied to the C–C bond lengths and the C–C–C bond angles [7,8] of the hexane molecule. Hydrogen atoms were geometrically placed (d(C–H) 0.95 Å, $U(\text{iso})_H$ =

1.15 $U(\mathrm{iso})_C$) and allowed to "ride" on the carbon atoms to which they were bonded, with the shifts in the isotropic temperature factor made equal to that of the bonded carbon. Owing to the low number of observed reflections only the rhenium and phosphorus atoms were assigned anisotropic thermal parameters. In addition, one overall isotropic thermal parameter was assigned to both the inner and outer carbon atoms of the pentamethylcyclopentadienyl rings respectively. For each individual cyclohexyl ring similar carbon atoms were assigned equivalent temperature factors. One overall temperature factor was assigned to the hexane molecule.

The final residuals were $R = 0.063$, and $R_w = 0.053$, and the goodness of fit was 1.069. Refinement was by full-matrix least-squares minimising the function

Table 2

Atomic coordinates ($\times 10^4$) and U_{eq} or U(iso) (Å^2)($\times 10^4$) with e.s.d.'s in parentheses for the non hydrogen atoms in **3**.

Atom	x/a	y/b	z/c	$U_{eq}/U(\mathrm{iso})$
Re(1)	2242(1)	2004.0(6)	4370.2(8)	324
P(1)	3783(6)	2792(3)	4220(4)	304
O(1)	727(17)	2378(9)	2536(13)	686(57)
C(1)	1389(21)	2209(11)	3291(16)	421(71)
C(11)	475(24)	1603(12)	4754(17)	398(32)
C(12)	688(23)	2297(11)	5145(16)	398(32)
C(13)	1770(23)	2264(11)	5782(17)	398(32)
C(14)	2354(22)	1651(12)	5910(17)	398(32)
C(15)	1515(22)	1252(12)	5236(16)	398(32)
C(16)	−693(25)	1318(14)	4155(19)	681(39)
C(17)	−305(24)	2797(12)	4913(17)	681(39)
C(18)	2202(23)	2854(13)	6412(16)	681(39)
C(19)	3507(24)	1459(14)	6654(18)	681(39)
C(20)	1662(25)	510(12)	5266(19)	681(39)
C(21)	4275(17)	1974(15)	4075(13)	344(53)
C(22)	5241(23)	1630(10)	4733(17)	423(49)
C(23)	5256(23)	897(11)	4763(16)	389(47)
C(24)	5462(22)	693(12)	3771(16)	480(71)
C(25)	4519(22)	1010(10)	3037(16)	389(47)
C(26)	4444(23)	1758(10)	3108(15)	423(49)
C(31)	3515(19)	3287(10)	3170(15)	292(60)
C(32)	4694(21)	3587(12)	2871(16)	426(49)
C(33)	4338(25)	3873(13)	1877(18)	645(60)
C(34)	3284(23)	4348(13)	1836(18)	579(80)
C(35)	2142(25)	4109(13)	2191(17)	645(60)
C(36)	2459(22)	3830(12)	3162(16)	426(49)
C(41)	4825(20)	3241(10)	5162(16)	351(68)
C(42)	4342(21)	3916(11)	5333(15)	396(47)
C(43)	5142(22)	4227(12)	6177(16)	482(51)
C(44)	6518(23)	4290(13)	6131(18)	579(79)
C(45)	7031(22)	3607(11)	5917(16)	482(51)
C(46)	6266(19)	3304(11)	5077(15)	396(47)
C(101)	342(28)	4830(9)	5433(15)	1273(96)
C(102)	1540(59)	5211(37)	5877(32)	1273(96)
C(103)	996(81)	5313(20)	6159(41)	1273(96)
C(104)	2057(27)	4977(18)	6843(17)	1273(96)

Table 3

Bond lengths (Å) and angles (deg) with e.s.d.'s in parentheses for **3**.

(a) Bond lengths			
Re(1)–P(1)	2.324(6)	C(21)–C(22)	1.46(3)
Re(1)–C(1)	1.75(2)	C(21)–C(26)	1.55(3)
Re(1)–C(11)	2.21(2)	C(22)–C(23)	1.49(3)
Re(1)–C(12)	2.26(2)	C(23)–C(24)	1.59(3)
Re(1)–C(13)	2.32(2)	C(24)–C(25)	1.48(3)
Re(1)–C(14)	2.39(2)	C(25)–C(26)	1.53(3)
Re(1)–C(15)	2.23(2)	C(31)–C(32)	1.53(3)
Re(1)–C(21)	2.27(2)	C(31)–C(36)	1.57(3)
P(1)–C(21)	1.77(3)	C(32)–C(33)	1.58(3)
P(1)–C(31)	1.84(2)	C(33)–C(34)	1.47(3)
P(1)–C(41)	1.86(2)	C(34)–C(35)	1.49(3)
O(1)–C(1)	1.26(2)	C(35)–C(36)	1.54(3)
C(11)–C(12)	1.53(3)	C(41)–C(42)	1.50(3)
C(11)–C(15)	1.39(3)	C(41)–C(46)	1.56(3)
C(11)–C(16)	1.50(3)	C(42)–C(43)	1.52(3)
C(12)–C(13)	1.35(3)	C(43)–C(44)	1.47(3)
C(12)–C(17)	1.46(3)	C(44)–C(45)	1.54(3)
C(13)–C(14)	1.39(3)	C(45)–C(46)	1.49(3)
C(13)–C(18)	1.54(3)	C(101)–C(101)′	1.52 [a]
C(14)–C(15)	1.46(3)	C(101)–C(102)	1.53 [a]
C(14)–C(19)	1.54(3)	C(101)–C(103)	1.53 [a]
C(15)–C(20)	1.51(3)	C(102)–C(104)	1.52 [a]
		C(103)–C(104)	1.53 [a]
(b) Bond angles			
C(1)–Re(1)–P(1)	89.8(7)	C(26)–C(21)–Re(1)	117.8(14)
C(21)–Re(1)–P(1)	45.2(8)	C(26)–C(21)–P(1)	117.9(17)
C(21)–Re(1)–C(1)	99.8(9)	C(26)–C(21)–C(22)	107.8(20)
C(21)–P(1)–Re(1)	65.9(7)	C(23)–C(22)–C(21)	120.2(22)
C(31)–P(1)–Re(1)	117.4(7)	C(24)–C(23)–C(22)	103.5(20)
C(31)–P(1)–C(21)	114.2(10)	C(25)–C(24)–C(23)	112.8(20)
C(41)–P(1)–Re(1)	126.2(7)	C(26)–C(25)–C(24)	114.6(20)
C(41)–P(1)–C(21)	114.1(9)	C(25)–C(26)–C(21)	111.3(20)
C(41)–P(1)–C(31)	110.8(10)	C(32)–C(31)–P(1)	117.6(15)
O(1)–C(1)–Re(1)	176.4(20)	C(36)–C(31)–P(1)	112.7(15)
C(15)–C(11)–C(12)	103.2(20)	C(36)–C(31)–C(32)	109.6(18)
C(16)–C(11)–C(12)	129.2(24)	C(33)–C(32)–C(31)	111.1(19)
C(16)–C(11)–C(15)	126.4(24)	C(34)–C(33)–C(32)	109.2(21)
C(13)–C(12)–C(11)	105.8(19)	C(35)–C(34)–C(33)	115.6(23)
C(17)–C(12)–C(11)	120.3(22)	C(36)–C(35)–C(34)	114.2(21)
C(17)–C(12)–C(13)	133.0(23)	C(35)–C(36)–C(31)	107.2(20)
C(14)–C(13)–C(12)	116.0(21)	C(42)–C(41)–P(1)	113.9(15)
C(18)–C(13)–C(12)	120.7(22)	C(46)–C(41)–P(1)	115.4(15)
C(18)–C(13)–C(14)	122.8(23)	C(46)–C(41)–C(42)	107.9(17)
C(15)–C(14)–C(13)	101.9(20)	C(43)–C(42)–C(41)	111.6(19)
C(19)–C(14)–C(13)	126.7(23)	C(44)–C(43)–C(42)	113.4(21)
C(19)–C(14)–C(15)	131.1(22)	C(45)–C(44)–C(43)	108.6(21)
C(14)–C(15)–C(11)	113.1(22)	C(46)–C(45)–C(44)	112.9(20)
C(20)–C(15)–C(11)	126.2(23)	C(45)–C(46)–C(41)	110.4(18)
C(20)–C(15)–C(14)	119.1(22)	C(102)–C(101)–C(101)′	111.4 [a]
P(1)–C(21)–Re(1)	68.9(7)	C(103)–C(101)–C(101)′	113.2 [a]
C(22)–C(21)–Re(1)	116.7(16)	C(104)–C(102)–C(101)	112.1 [a]
C(22)–C(21)–P(1)	123.6(17)	C(104)–C(103)–C(101)	111.5 [a]

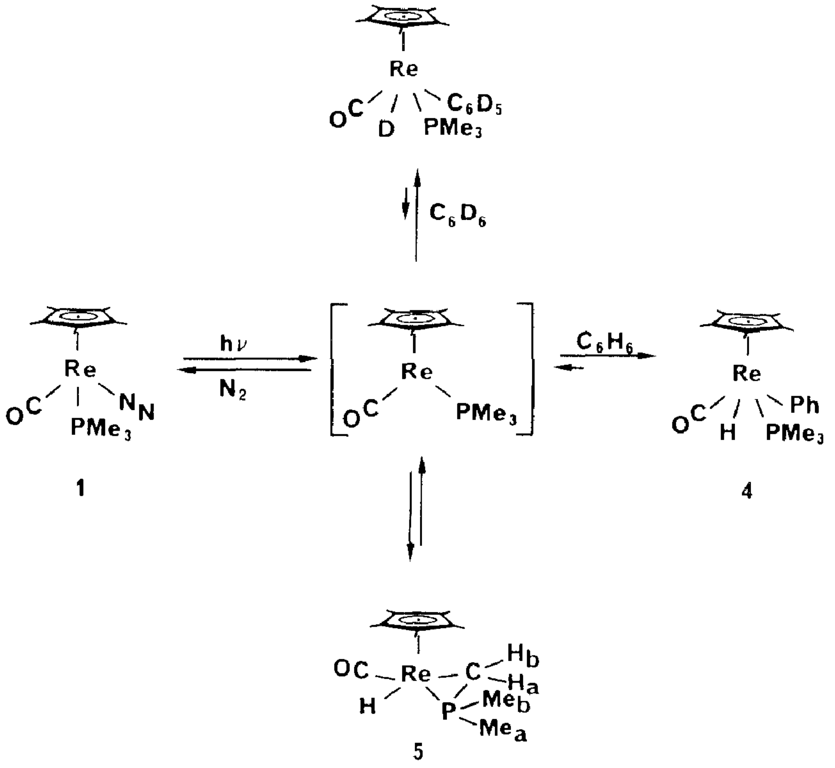
[a] A restraint was applied to this bond or bond angle.

$\Sigma w(|F_o| - |F_c|)^2$, where w was calculated from a three term Chebyshev series so that $w = [0.699t_0(x) + 0.308t_1(x) + 0.637t_2(x)]^{-1}$, where $x = F_o/F_{max}$ [9]. The refinement was considered complete when the ratio of all shifts to e.s.d.'s was less than 0.1. The highest peak in the final difference map was 1.74(12) e Å^{-3} and was situated 1.11 Å from the rhenium atom. Complex neutral atom scattering factors were taken from International Tables for Crystallography [10]. Calculations were carried out on a Microvax II computer with use of the NRC VAX Crystal Structure System [11] and the CRYSTALS suite of programs [12]. Positional parameters are given in Table 2. Selected bond distances and angles are listed in Table 3. Anisotropic thermal parameters, hydrogen atom coordinates, mean plane calculations, and a table of calculated and observed structure factors are available from the authors.

Results

(a) Irradiation of $Cp^\star Re(CO)(PMe_3)(N_2)$ (1)

UV irradiation of **1** in benzene solution at room temperature for only 10 min resulted in quantitative conversion to a single carbonyl containing product. This was isolated from hexane at −78 °C as a white solid and was characterized by spectroscopy and analysis as the benzene C–H activation product *trans*-(H,Ph)-$Cp^\star Re(CO)(PMe_3)(H)(Ph)$ (4) (Scheme 1). This compound is air-sensitive, but stable as a solid and in hexane solution under N_2 at low temperature (−15 to



Scheme 1

$-78\,°$C). Solid samples can be stored at $-15\,°$C under N_2 atmosphere in the freezer for several months without visible deterioration. It is very soluble in benzene, hexane and cyclohexane. It also dissolves in $CHCl_3$ and $CHBr_3$ but gives orange-red solutions which have been identified as the corresponding *cis*-dihalide complexes, *cis*-$Cp^\star Re(CO)(PMe_3)Cl_2$ and *cis*-$Cp^\star Re(CO)(PMe_3)Br_2$ respectively [13]. When dissolved in C_6D_6, about 20% exchange of bound C_6H_6 with bulk solvent was determined by ^1H NMR and MS during six days at $8\,°$C. A complete regeneration of the parent dinitrogen complex **1** was observed when a hexane solution was pressurized to 2000 psi with N_2 for 12 h.

The IR spectrum of **4** shows a strong and quite broad ν(CO) absorption at 1872 cm^{-1} in benzene and a sharp absorption at 1889 cm^{-1} in hexane. The presence of the hydride and phenyl ligands was clearly observed in the ^1H NMR spectrum. The resonance for the former appears as a doublet at δ -9.18 with ^2J(PH) 66.7 Hz and integrates for 1H. For the latter a multiplet at δ 7.16 with a relative intensity of 3H is tentatively assigned to *meta* and *para* protons, and a second multiplet, at much lower field (δ 7.96) and with a relative intensity of 2H, is assigned to the *ortho* protons. The ^{13}C NMR spectrum also demonstrates the presence of the phenyl ligand. The ^{13}C resonances appeared in the 123–147 ppm region and the assignment of each resonance was made on the basis of carbon couplings to phosphorus and protons (see Experimental section). the carbonyl carbon resonance was observed at δ 209.02 as a doublet in the proton coupled spectrum and as a singlet in the decoupled spectrum.

The electron-impact MS at 12 eV clearly showed the molecular ion at m/z 504, and a base peak at m/z 426 resulting from the reductive elimination of benzene. At much higher energy (70 eV) the molecular ion could not be observed. Instead, the MS showed peaks at m/z 502, 474 and 426 which appear to indicate $Cp^\star Re(CO)(PMe_3)_2$ formed upon decomposition.

The assignment of mutually *trans* hydride and phenyl groups in **4** is based on the following results. The ^2J(PH) value for the the hydride resonance (66.7 Hz) indicates *cis*-hydride and PMe_3 groups. This value is in good agreement with those observed in the hydridohalide derivatives $Cp^\star Re(CO)(PMe_3)(H)(X)$ which also possess a *cis*-H–Re–PMe_3 moiety [1,13], and in the complexes *cis*-$CpMo(CO)_2(PR_3)(H)$ (^2J(PH) 64–67 Hz) [14]. For the CO group, a value of ^2J(CH) 10.8 Hz was observed in the ^{13}C NMR spectrum and no observable coupling to phosphorus; this indicates that the CO is *cis* to the hydride and *trans* to the PMe_3 group. The value of ^2J(CH) is in good agreement with that observed in *trans*-(H,Br)-$Cp^\star Re(CO)_2(H)(Br)$ (^2J(CH) 13.6 Hz) [13]. Furthermore, a strong NOE enhancement of the hydride and phenyl resonances resulted from irradiation of the PMe_3 proton signal.

Photolysis of **1** in hexane or cyclohexane for 10 min resulted in the complete disappearance of the dinitrogen complex and the formation of a single carbonyl containing product showing a very strong and sharp ν(CO) at 1878 cm^{-1}. The product was isolated at $-78\,°$C as a white solid and was characterized as the cyclometallated complex *trans*-(H,CH_2)-$Cp^\star Re(\eta^2\text{-}CH_2PMe_2)(H)(CO)$ (**5**) resulting from the intramolecular C–H activation of a methyl group of the PMe_3 ligand (Scheme 1).

Compound **5** is very air-sensitive. It is very soluble in hexane and cyclohexane, and quite stable under N_2 at low temperature in those solvents. However, it reacted slowly with benzene or C_6D_6 in the dark to form *trans*-(H,Ph)-$Cp^\star Re(CO)(PMe_3)$-

(H)(Ph) and Cp*Re(CO)(PMe$_3$)(D)(C$_6$D$_5$), respectively. Likewise, it reacted with N$_2$ under 2000 psi of pressure to produce quantitatively the parent dinitrogen complex **1**. However, it did not react with CH$_4$ (500 psi) at room temperature. The ^{1}H NMR spectrum of **5** shows a doublet at δ −9.92, ^2J(PH) 38.2 Hz with a relative intensity of 1H, which is assigned to the hydride resonance. Two doublets of doublets at δ −0.57 and 0.57 (each integrating for 1H) are assigned to the two non-equivalent methylene protons H$_b$ and H$_a$ respectively. Likewise, the two doublets at δ 1.37 (3H) and 1.55 (3H) are assigned to the two non-equivalent methyl groups Me$_b$ and Me$_a$. The resonance for the Cp* protons appears at δ 2.02 with a relative intensity of 15H. The instability of this compound in C$_6$D$_6$ and cyclohexane-d_{12} over the time required for data collection has so far precluded accurate measurement of the ^{13}C NMR spectrum. By analogy with Cp*Re(CO)(PMe$_3$)(H)(Ph) (**4**) and on the basis of ^{1}H NMR and NOE results, we believe that **2** possesses a *trans* stereochemistry; that is, the hydride is *trans* to the methylene carbon and *cis* to P. NOE experiments have allowed us to assign the non-equivalent methyl groups and methylene protons of the cyclometallated fragment in **5**. The NOE results are summarized as follows: irradiation of Me$_b$ enhanced H$_b$ more strongly than H$_a$; irradiation of Me$_a$ enhanced H$_a$ more strongly than H$_b$; irradiation of Cp* enhanced H$_b$ and Me$_b$ much more strongly than it did H$_a$ and Me$_a$. Irradiation of either Me$_a$ or Me$_b$ gave enhancement of hydride (more strongly with Me$_a$), as did irradiation of H$_a$, but not H$_b$. This suggests that the hydride is *cis* to PMe$_2$ and *trans* to CH$_2$.

Compound **5** was also characterized by electron-impact MS at 12 eV, which exhibits the molecular ion at m/z 426 as the highest mass peak. As with the hydridophenyl complex, the spectrum at 70 eV shows peaks at m/z 502, 474 and 426.

Irradiation of **1** in hexane, in the presence of methane or molecular hydrogen did not give the unknown hydridomethyl Cp*Re(CO)(PMe$_3$)(H)(Me) or dihydride Cp*Re(CO)(PMe$_3$)H$_2$ complexes. Instead, **5** was the only product. This result contrasts with the formation of the known [15] dihydride complex *trans*-Cp*Re(CO)$_2$H$_2$ when the dicarbonyldinitrogen complex Cp*Re(CO)$_2$(N$_2$) was irradiated in hexane with H$_2$ purge. Irradiation of Cp*Re(CO)$_2$(N$_2$) in hexane with CH$_4$ purge gave a mixture of Cp$_2^\star$Re$_2$(CO)$_3$ and Cp$_2^\star$Re$_2$(CO)$_5$ [16].

(b) Irradiation of Cp*Re(CO)(P{C$_6$H$_{11}$}$_3$)(N$_2$) (2)

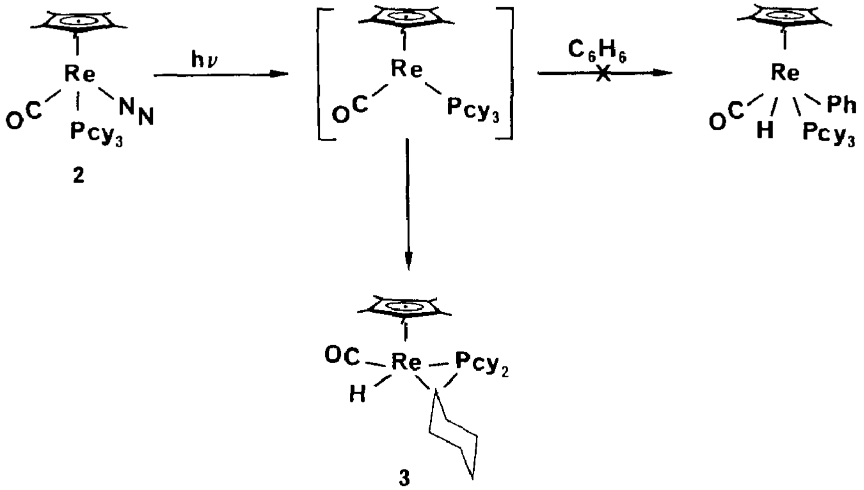
The UV-irradiation of **2** in benzene for 10 min at 0 °C in both Pyrex and quartz photolysis tubes results in the complete disappearance of the starting dinitrogen complex and only a single carbonyl absorption at 1836 cm^{-1}. Following isolation, the ^{1}H NMR spectrum in benzene-d_6 of the product of reaction shows the presence of only a single hydride product. Coupling between the hydride and phosphorus atom thought to be coordinated to the central rhenium atom, as seen in the C–H activation products resulting from the irradiation of the trimethylphosphinedinitrogen complex **1**, is surprisingly absent; the hydride is a singlet at δ −8.64 ppm. As well, a sharp resonance at δ 2.07 ppm and a complex pattern of multiplets in the δ 1 to 2 ppm region are assigned to the hydrogens in the C$_5$Me$_5$ and P(C$_6$H$_{11}$)$_3$ groups respectively on the basis of approximate integration. A resonance at δ 7.22 ppm is assumed to be totally due to the residual protons in the deuterated solvent; to be sure of this, the ^{1}H NMR of this product was also recorded in acetone-d_6 and no such resonance was observed. This indicated that the irradiation of **2** did not lead to the activation of the carbon–hydrogen bonds in benzene. Interestingly, the hydride resonance is shifted significantly upfield in acetone-d_6 to δ -9.1 ppm, while the chemical shifts of the hydrogens in the other groups in the product remained essentially the same as in benzene-d_6.

Complex **2** was then irradiated directly in benzene-d_6 in an NMR tube under nitrogen for 10 min at 0 °C. The IR spectrum again showed the complete disappearance of **2** and production of only one carbonyl absorption at 1834 cm^{-1}. The ^1H NMR spectrum of the solution again showed the presence of only one hydride resonance at δ -8.66 ppm along with a single peak at δ 2.06 ppm (C_5Me_5) and a complex multiplet pattern in the δ 1–2 ppm region ("Pcy_3"). If intermolecular activation of a carbon–deuterium bond in C_6D_6 had occurred now no hydride resonance would be expected in the ^1H NMR spectrum. Since the observed spectrum for this reaction was identical with that found for the irradiation of **2** in benzene, clearly no intermolecular C–H activation of benzene has occurred.

UV irradiation of the complex **2** in cyclohexane for 10 min at 0 °C also resulted in a single carbonyl absorption, this time at 1850 cm^{-1}. The ^1H NMR of this product in benzene-d_6 gave a spectrum identical to those found for the products of irradiation in benzene and benzene-d_6. Once again, a single hydride resonance was observed at δ -8.64 ppm. Also, a ^1H NMR spectrum was recorded in acetone-d_6 for comparison with the spectrum of the product of irradiation in benzene also recorded in this solvent. Again, the hydride was shifted upfield to δ -9.1 ppm while the chemical shift of C_5Me_5 and "Pcy_3" groups remained essentially the same as in the benzene-d_6 spectrum.

The irradiation of **2** in benzene, benzene-d_6, and cyclohexane clearly give the same product **3** (Scheme 2). There is no evidence for the C–H activation of the carbon–hydrogen bonds of benzene as shown by the absence of resonances in the phenyl region of the spectra recorded in acetone-d_6, and by the production of the same hydride product upon irradiation in benzene-d_6.

The product **3** was finally synthesized on a preparative scale in 60.0% yield for additional analysis. Both the mass spectrum (at 12 eV) and the chemical analysis



Scheme 2

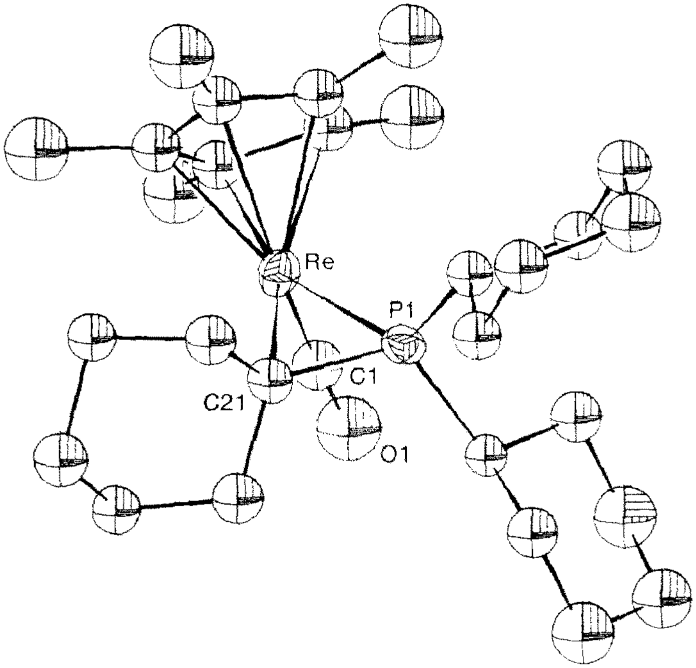


Fig. 1. Perspective view of a molecule of $Cp^{\star}Re(\eta^2\text{-}C_6H_{10}P\{C_6H_{11}\}_2)(H)(CO)$ (3).

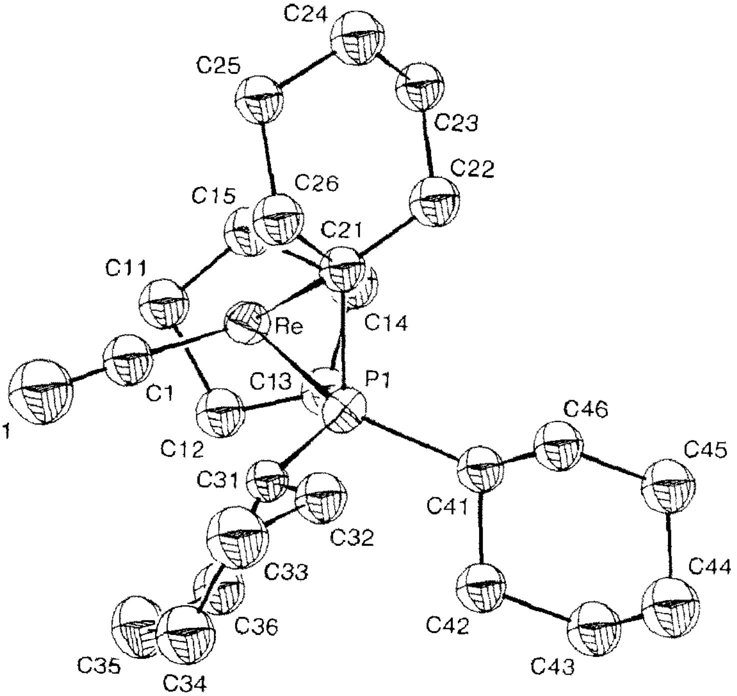


Fig. 2. View of 3 projected onto the C_5Me_5 ring. The hydride ligand is considered to occupy the "vacant" coordination site between C(1) and C(21). Methyl groups are omitted for clarity.

gave additional evidence for the production of an internally cyclometallated product. The molecular ion peak in the mass spectrum at *m/z* 630 corresponds to the molecular formula: (η^5-C_5Me_5)Re(CO)(Pcy_3). The fragmentation pattern clearly shows the sequential loss of two C_6H_{10} fragments indicating the coordination of the tricyclohexylphosphine ligand in some manner to the metal. In addition, there were no peaks at all near *m/z* 708 corresponding to the formula: (η^5-C_5Me_5)Re(CO)(Pcy_3)(Ph)(H).

The low temperature (212 K) structure determination of compound **3** was successfully obtained despite the availability of only rather poor quality crystals from crystallization from hexane at −78 °C. The structure consists of discrete molecules of **3** and hexane of solvation in 2/1 ratio. Two views of a molecule of **3** are given in Figs. 1 and 2. The hydride ligand, known to be present from the ^{1}H NMR spectrum, was not located. The view in Fig. 2, and a perusal of the interbond angles, where P(1)–Re(1)–C(1) (89.8°) is more acute than C(1)–Re(1)–C(21), indicate the logical site for the hydride to be between C(1) and C(21), i.e., pseudo-*trans* to P(1) in a typical four-legged piano-stool configuration.

The main feature of interest in the structure is the cyclometallated tricyclohexylphosphine ligand. The *ipso* C–H bond of one C_6H_{11} ring has been oxidatively added to rhenium to produce a 3-membered metallacycle $\overline{\text{Re–P(1)–C(21)}}$. The hydride ligand is positioned *cis* to the carbon atom C(21). While the rather large standard deviations in bond lengths do not allow reliable conclusions to be drawn there is an indication that the P(1)–C(21) bond length (1.77(3) Å) in the metallacycle is probably shorter than the other two external P(1)–C(31) and P(1)–C(41) bond lengths (1.84(2) Å and 1.86(2) Å, respectively) [17*,18–20]. The P(1)–C(21) bond is oriented more-or-less parallel to the Cp* plane, as we have typically found in other related η^5-C_5H_5 or η^5-C_5Me_5 rhenium carbonyl complexes possessing 3-membered metallacycles formed with PhC≡CPh [21], PhN=NPh [22] or mesityl oxide [23].

Discussion

Irradiation of Cp*Re(CO)(PMe_3)(N_2) (**1**) or Cp*Re(CO)(Pcy_3)(N_2) (**2**) in cyclohexane causes rapid loss of N_2 and presumably the formation of the (unobserved) coordinatively unsaturated intermediates "Cp*Re(CO)(PMe_3)" and "Cp*-Re(CO)(Pcy_3)" (Schemes 1 and 2). The photochemical extrusion of N_2 has ample precedent in other systems [24–27]. These intermediates do not attack cyclohexane but undergo internal cyclometallation. In the case of the tricyclohexylphosphine complex the solution IR and ^{1}H NMR spectra indicate that a single product **3** is formed, and the X-ray structure determination of **3** shows that the cyclometallation has occurred at the *ipso* carbon atom C(21) of one cyclohexyl ring with the formation of a 3-membered metallacycle.

The hydride resonance at δ −8.64 in C_6D_6 exhibits no observable coupling to P (compare the PMe_3 derivative **5**); the interbond angles are consistent with the hydride occupying a position *trans* to P and *cis* to the metal–bound carbon atom C(21). Complex **3** thus has the geometry anticipated for a concerted oxidative

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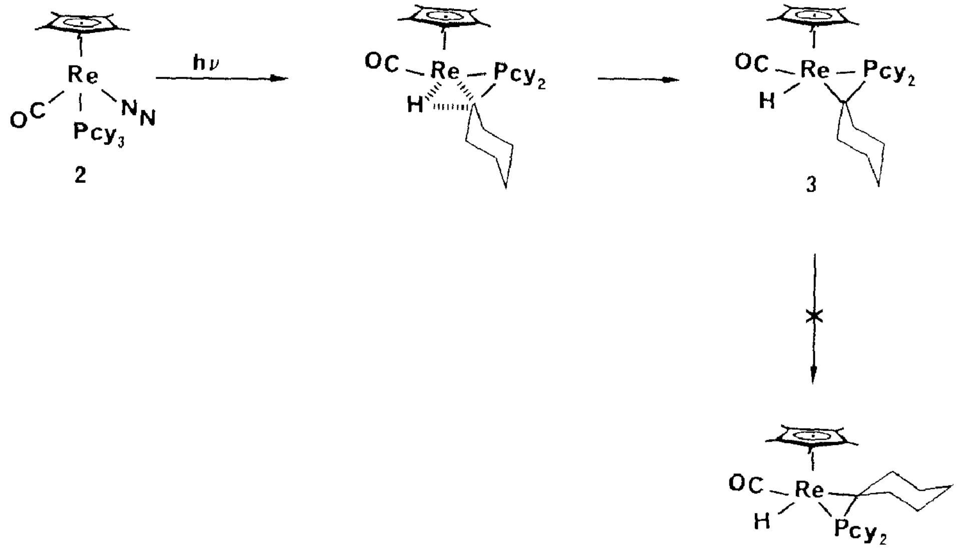
* Reference number with asterisk indicates a note in the list of references.

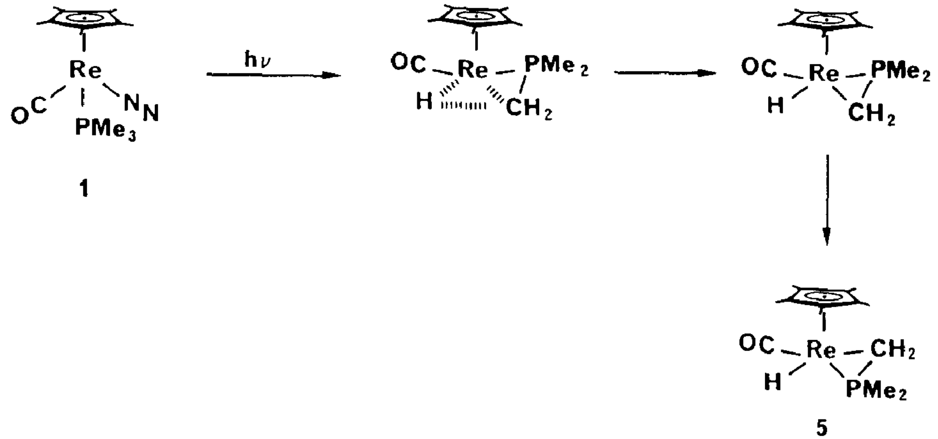


Scheme 3

addition of the C–H bond (Scheme 3). There is no evidence, that we can detect, of isomerization to the *trans*-(H,C) isomer.

It is of interest that metallation has occurred as the *ipso* carbon atom rather than at the adjacent 2- or 6- carbon positions which would have generated a four-membered ring. Our survey of the previous literature has not revealed any other account of cyclometallation of a tricyclohexylphosphine ligand with which to compare this result. However, cyclometallations of aromatic phosphine ligands, e.g., triphenylphosphine, commonly produce the four-membered metallacycle [28*]. The partial exchange of hydrogens of tricyclohexylphosphine ligands in $RuH_4(Pcy_3)_3$ with deuterated aromatic solvents has been observed [29]. The extent of the exchange was consistent with exchange of the hydrogen on C_1 and the axial hydrogens on C_2 and C_6 and presumably involves intermediates in which C–H oxidative addition at each of these sites has occurred, though none was observed directly. The thermal decomposition of *trans*-chloro(1-norbornylmethyl)bis(tricyclopentylphosphine)platinum(II) has been described to yield a product containing the cyclometallated tricyclopentylphosphine ligand. This was not fully characterized, but was considered likely to contain the four-membered rather than 3-membered metallacycle [30]. Most interestingly, the coordinatively unsaturated complex $Pt(cy_2PCH_2CH_2Pcy_2)$ which is active in numerous intermolecular C–H activation reactions, does not appear to undergo internal cyclometallation of a cyclohexyl group [31]. On the basis of the crystal structure of a Pt^{II} precursor, it is thought possible that this is because the cyclohexyl groups are folded back from the platinum centre so there are no significant non-bonded interactions between Pt and cyclohexyl C–H bonds. An additional factor would be the observed increased resistance of chelating bis(phosphine) complexes toward metallation compared with monodentate ones [32].

Irradiation of the trimethylphosphine complex **1** in cyclohexane also produces an internally cyclometallated product **5** which has been fully characterized by spectroscopy. Unfortunately, X-ray quality crystals could not be obtained from the low temperature crystallization [33*,34*,35–43]. The structure of **5** contrasts with that



Scheme 4

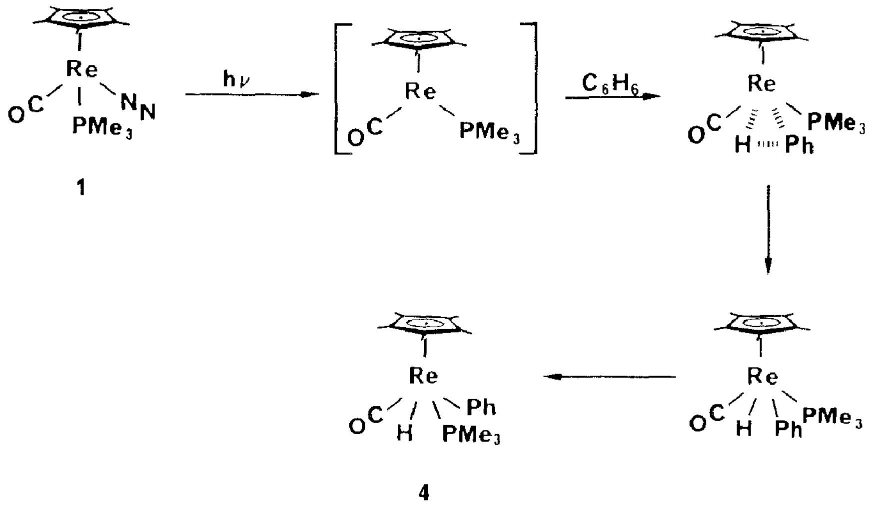
of **3** in that the hydride ligand is *trans* to the cyclometallated carbon atom, on the basis of detailed NOE experiments, and the value of ^2J(PH) 38.2 Hz indicating mutually *cis* hydride and phosphorus. Thus **5** does not have the structure appropriate to the expected product of concerted C–H addition **5a**, but is presumably the thermodynamically more stable isomer (Scheme 4). Possibly **3** is unable to undergo this rearrangement for steric reasons.

The behaviour of **1** and **2** when irradiated in benzene differs substantially. The PMe_3 complex **1** undergoes clean loss of N_2 and the formation of the single product of intermolecular C–H activation of benzene, *trans*-(H,Ph)-$Cp^\star Re(CO)(PMe_3)(H)(Ph)$ (**4**). The Pcy_3 complex **2** loses N_2, but no intermolecular C–H activation of benzene is observed; the product is the same cyclometallated complex **3** that is formed in cyclohexane. Thus the hoped-for increased tendency for intermolecular C–H activation anticipated in view of the greater basicity of **2** is not realized in practice. An over-riding consideration must be the increased steric demand of the tricyclohexylphosphine ligand (reflected in its larger cone angle [5]). Certainly, it has previously been demonstrated that internal metallation may be promoted by sterically demanding groups on the phosphine ligand [44]. However, there do not appear to have been any studies specifically of the role of tricyclohexylphosphine ligands in cyclometallation reactions [45*].

The structure of the benzene addition product **4** has the hydride ligand *trans* to the phenyl group, i.e., the configuration is similar to that of **5**, and again is presumed to be a rearrangement from a first-formed *cis* product (Scheme 5).

These configurations assigned to **4** and **5** are consistent with the configurations assigned by Bergman and co-workers to the identical complexes formed in the photolysis of $Cp^\star Re(CO)_2(PMe_3)$ or $Cp^\star Re(CO)(PMe_3)_2$ [3] and closely related complexes $CpRe(\eta^2\text{-}CH_2PMe_2)(PMe_3)(H)$ and $CpRe(PMe_3)_2(H)(Ph)$ formed in the photolysis of $CpRe(PMe_3)_3$ [3,43].

The observed reactions of **4** and **5** indicate that the steps in Scheme 1 are reversible under non-photochemical conditions. Thus, the reaction of **5** with benzene to give **4** and with nitrogen to regenerate the dinitrogen complex **1** are most likely accounted for by reaction of coordinatively unsaturated "$Cp^\star Re(CO)(PMe_3)$" present in equilibrium with **5** in solution. This intermediate was not present in



Scheme 5

sufficient concentration to be observed directly in the IR or NMR spectra of **5**. Furthermore, as described above, satisfactory NOE difference spectra for **5** could be obtained, so that the equilibration with "Cp*Re(CO)(PMe$_3$)" (and possible scrambling of H, CH_2 and PMe_2 protons of **5** that would be expected to result from this) was not sufficiently rapid to interfere. Reaction of **5** with C_6D_6, if it proceeds through the actual reaction of "Cp*Re(CO)(PMe$_3$)" with C_6D_6 as envisaged, would result in the rhenium-deuteride Cp*Re(CO)(PMe$_3$)(D)(C_6D_5), but no rhenium–hydride bond. This is exactly as observed. The ^1H NMR of **5** in C_6D_6 shows the growth of the characteristic resonances at δ 1.08 (d, ^2J(PH) 8.9 Hz, PMe_3) and 1.81 (s, C_5Me_5) typical of **4**, but no corresponding hydride or phenyl resonances. Complex **4** itself undergoes exchange with C_6D_6 and regeneration of dinitrogen complex **1** under N_2 pressure. These reactions are most simply accounted for by non-photochemical reductive elimination of C_6H_6 from **4** (possibly via an intermediate η^2-benzene complex [46]) to give the same unsaturated intermediate "Cp*Re(CO)(PMe$_3$)". In the case of Cp*Re(CO)(Pcy$_3$)(N_2) (**2**) we presume (Scheme 2) that loss of N_2 occurs on irradiation to give "Cp*Re(CO)(Pcy$_3$)" before cyclometallation occurs. But unlike **5** this cyclometallated cyclohexylphosphine complex **3** does not undergo transformation to a corresponding phenyl hydrido complex in benzene, so we have no additional evidence for the participation of this unsaturated complex in the chemistry of **3**.

Studies of these, and other rhenium phosphine dinitrogen complexes [2] as C–H activation precursors, are continuing.

Acknowledgments

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