η^5 to η^1 Conversions of Indenyltricarbonylrhenium

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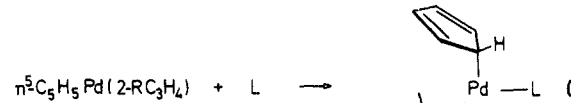
The reaction of $(\eta^5\text{-}C_9H_7)Re(CO)_3$, **6**, with PMe_3 produces *fac*-$(\eta^1\text{-}C_9H_7)Re(CO)_3(PMe_3)_2$, **7**, in high yield. The rate of reaction is greatly accelerated compared to that for $(\eta^5\text{-}C_5H_5)Re(CO)_3$, **3**, and PMe_3. **6** also reacts with $P(n\text{-}Bu)_3$ and 2,2′-bipyridyl to give η^1-indenyl–bis(phosphine) adduct **10** and η^1-indenyl–bipyridyl adduct **13**, respectively. Complexes **7**, **10**, and **13** all undergo degenerate intramolecular 1,3 rhenium migrations on the NMR time scale at 25 °C. The fluxionality is frozen out at low temperature. **6** reacts with H_2O and acetone at 88 °C to give $[Re(CO)_3OH]_4 \cdot 2[C_9H_7C(CH_3)_2OH]$, **14**.

Introduction

Basolo first proposed η^5-cyclopentadienyl ring slippage to explain the rapid second-order substitution reaction of PPh_3 and $(\eta^5\text{-}C_5H_5)Rh(CO)_2$.[1] In 1980, Werner reported the first example of the conversion of an $\eta^5\text{-}C_5H_5$ to an isolable $\eta^1\text{-}C_5H_5$ complex. He found that reaction of $(\eta^5\text{-}C_5H_5)Pd(2\text{-}RC_3H_4)$ and $P(i\text{-}Pr)_3$ produces a mixture of $(\eta^5\text{-}C_5H_5)Pd(\eta^1\text{-}2\text{-}RC_3H_4)P(i\text{-}Pr)_3$ and $(\eta^1\text{-}C_5H_5)Pd(\eta^3\text{-}2\text{-}RC_3H_4)P(i\text{-}Pr)_3$ (eq 1).[2] At about the same time we independently found that $(\eta^5\text{-}C_5H_5)Re(CO)(NO)(CH_3)$, **1**, reacts rapidly with PMe_3 to form the stable ring-slippage product $(\eta^1\text{-}C_5H_5)Re(CO)(NO)(CH_3)(PMe_3)_2$, **2**.[3] Since



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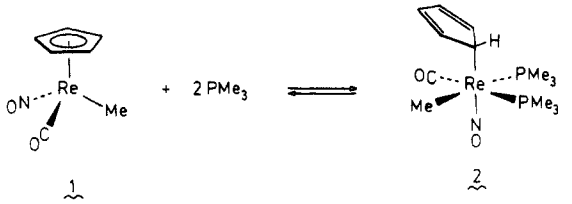
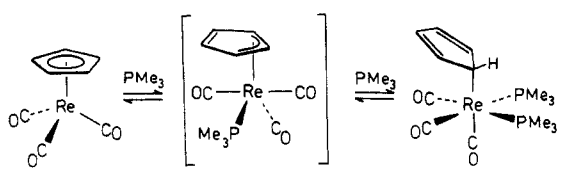


1 2

then, there have been a growing number of reports of $\eta^5\text{-}C_5H_5$ to $\eta^1\text{-}C_5H_5$ conversions.[4] In a recent paper, we reported the reaction of $(\eta^5\text{-}C_5H_5)Re(CO)_3$, **3**, with PMe_3 produces *fac*-$(\eta^1\text{-}C_5H_5)Re(CO)_3(PMe_3)_2$, **4**.[4b] The rate of reaction of **3** depended on the concentration of both Re and PMe_3; this requires requires an intermediate mono(phosphine) adduct. The only reasonable 18-electron structure for this intermediate is the $\eta^3\text{-}C_5H_5$ complex **5**.



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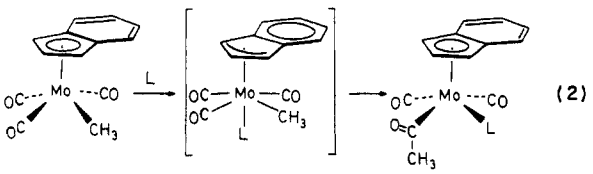
We have been unable to directly observe the $\eta^3\text{-}C_5H_5$ complex **5**. Apparently, the reaction of **5** with PMe_3 to give the $\eta^1\text{-}C_5H_5$ bis(phosphine) adduct **4** is much faster than the rate of formation of **5** from PMe_3 and **3**. In an effort to directly observe an $\eta^3\text{-}C_5H_5$ metal complex, we have sought a substituted $\eta^5\text{-}C_5H_5$ compound which would show enhanced reactivity with PMe_3 but which would produce an $\eta^3\text{-}C_5H_5$ which is no more reactive toward PMe_3 than **5**. The η^5-indenyl system is an excellent choice for such a system since in the conversion of the η^5-indenyl to an η^3-indenyl system, the full aromaticity of the benzene ring is achieved. More rapid substitution reactions of η^5-indenyl systems compared with η^5-cyclopentadienyl systems were first observed by Mawby for the reaction of $(\eta^5\text{-}C_9H_7)Mo(CO)_3CH_3$ and PPh_3 which gave the phosphine-substituted acyl complex $(\eta^5\text{-}C_9H_7)Mo(CO)_2(PPh_3)(COCH_3)$ (eq 2).[5] The rate of reaction was 10 times faster than that



(2)

for the analogous $\eta^5\text{-}C_5H_5$ complex. To explain the rate acceleration and the observed second-order kinetics, an η^3-indenyl intermediate was proposed. Subsequently, similar rapid substitution of η^5-indenyl complexes has been seen in a number of systems.[6] Recently Basolo reported a 10^8 rate enhancement for the second-order phosphine substitution reaction of $(\eta^5\text{-indenyl})Rh(CO)_2$ compared with $(\eta^5\text{-}C_5H_5)Rh(CO)_2$.[6g-i]

Here we report our attempt to observe an η^3 intermediate in the reaction of $(\eta^5\text{-}C_9H_7)Re(CO)_3$, **6**, with PMe_3. Although we were unable to directly detect an $\eta^3\text{-}C_9H_7$ species, dramatic effects of the indenyl group on the η^5 to η^1 conversion chemistry were noted. The rate of formation of a bis(phosphine) η^1 complex was much faster for η^5-indenyl complex **6** than for η^5-cyclopentadienyl complex **3**. The equilibrium between η^5 and η^1 complexes lies much farther toward the η^1 complex for the indenyl system than

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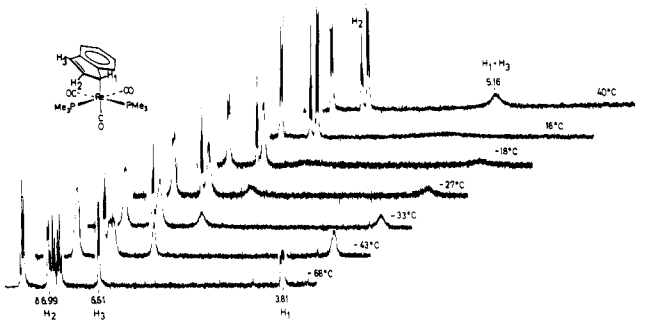
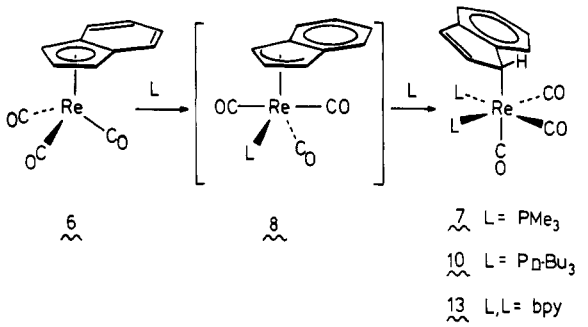


Figure 1. Variable-temperature 270-MHz ^1H NMR spectrum of **7**: indenyl ligand resonances.

for the cyclopentadienyl system. The high kinetic reactivity of η^5-indenyl complex **6** and the high thermodynamic stability of the η^1-indenyl products has allowed us to observe $\eta^5 \rightarrow \eta^1$ conversions driven even by the bulky $P(n\text{-}C_4H_9)_3 \equiv (PBu_3)$ ligand and by the less nucleophilic 2,2′-bipyridyl (bpy) ligand.[7]

Results

The reaction of excess 0.17 M PMe_3 with a slurry of $(\eta^5\text{-}C_9H_7)Re(CO)_3$, **6**, in hexane at room temperature produced η^1-indenyl compound **7** which was isolated as a white solid in 95% yield. The facial configuration of **7** is fully



6 **8**

7 L = PMe_3

10 L = $P\text{-}nBu_3$

13 L,L = bpy

supported by spectroscopic evidence and is analogous to *fac*-$(\eta^1\text{-}C_5H_5)Re(CO)_3(PMe_3)_2$, **4**, whose structure was established by X-ray crystallography.[4b] The IR spectrum of **7** has three CO bands at 2021, 1936, and 1894 cm^{-1} which show similar intensity ratios to the 2014, 1935, and 1890 cm^{-1} bands of **4**. As detailed below, rhenium undergoes a degenerate intramolecular 1,3 migration on the indenyl ligand that is fast on the NMR time scale at room temperatue and slow on the NMR time scale at −65 °C. In the ^1H NMR of **7** at −65 °C, no fluxionality of the η^1-C_9H_7 ligand of **7** was seen. The proton on the carbon bonded directly to rhenium appears at δ 3.81 and establishes the η^1 nature of **7**; the diastereotopic PMe_3 ligands of **7** gave rise to two doublets at δ 1.74 and 1.57; the six remaining nonequivalent indenyl hydrogens gave rise to three multiplets between δ 7.40 and 6.37. In agreement with the facial configuration of **7**, two ^{31}P resonances are seen at δ −43.1 and −46.6 at −70 °C for the two diastereotopic PMe_3 ligands; these resonances coalesce to a single broad resonance at δ −44.5 at +27 °C where the fluxional process exchanges the environment of the phosphine ligands. The alternate meridinal configuration with trans phosphines, which would have given rise to a single phosphorus resonance at all temperatures[8] and the meridinal configuration

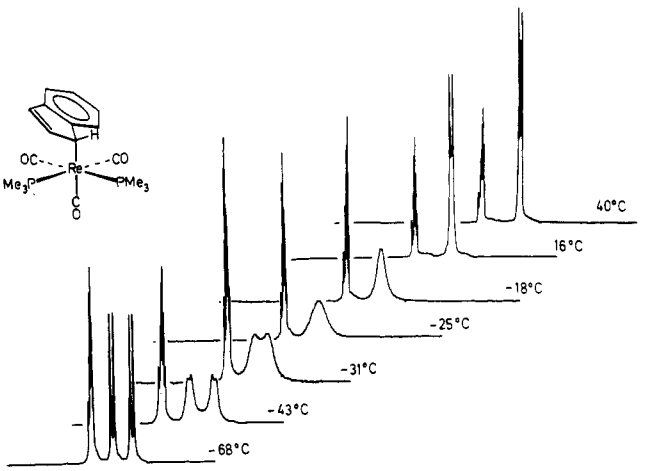


Figure 2. Variable-temperature 270-MHz ^1H NMR spectrum of **7**: PMe_3 ligand resonances.

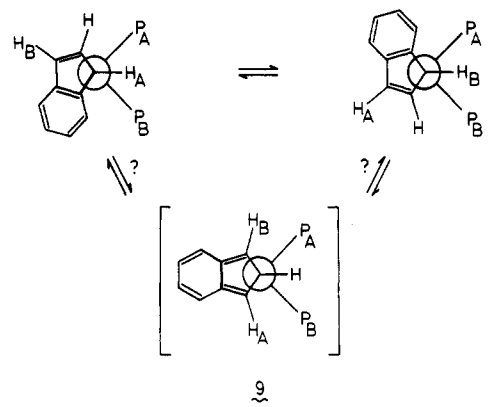


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Figure 3. View down Re–η^1-Indenyl Bond of **7**. Carbonyl ligands and methyl groups on phosphorus ligands are omitted for clarity.

with cis phosphines, which would have given rise to two resonances at all temperatures, can be excluded on the basis of temperature-dependent ^{31}P NMR.

The fluxional process which makes all five η^1-C_5H_5 protons in **4** equivalent is rapid on the NMR time scale even at −86 °C. In contrast, nonequivalence of the protons of the η^1-indenyl ligand of **7** begins to be seen in the ^1H NMR of **7** at +40 °C. The signals for H_1 and H_3 which are sharp multiplets at δ 3.81 and 6.31 at −68 °C begin to broaden at −43 °C, coalesce at about 16 °C, and appear as a broad singlet at 40 °C (Figure 1). The ABCD pattern of H_4, H_5, H_6, H_7 between δ 7.36 and 6.84 at −68 °C is also temperature dependent and is converted to a sharp AA′BB′ pattern at 16 °C. The signals due to the diastereotopic PMe_3 ligands of **7** are also temperature dependent and are transformed from two doublets at δ 1.86 and 1.69 at −68 °C to a virtually coupled triplet at δ 1.72 at 40 °C (Figure 2). This virtual coupling can occur only if the temperature-dependent process does not involve PMe_3 dissociation. $\Delta G^{\ddagger}$ for the fluxional process was calculated to be 12.0 ± 0.1 kcal mol^{-1} by comparison of simulated and observed spectra.[9] The barrier is substantially greater than the barrier for η^1-C_5H_5 compound **4** which is rapidly fluxional at −86 °C (estimated $\Delta G^{\ddagger} \leq 7$ kcal mol^{-1}). The larger barrier for η^1-indenyl systems compared with η^1-C_5H_5 systems has been observed previously; indeed, the

(7) To our knowledge the η^5-C_9H_7 to η^1-C_9H_7 conversions reported here represent the first examples of the conversion of an η^5-C_9H_7 complex into an isolable η^1-C_9H_7 complex. In 1977 Green reported that $Rh(C_2H_4)_2$-$(\eta^5\text{-}C_9H_7)$ reacts with excess *t*-BuNC to form $Rh(\sigma\text{-}C_9H_7)(t\text{-}BuNC)_4$ for which only infrared data was reported.[6e]

(8) This makes the resonable assumption that rotation about the long Re–indenyl bond is rapid at −60 °C.

(9) The computer simulation was done by using the computer program NMRSIM (written by M. Chen); the line width at half height (−68 °C) was taken to be 8.5 Hz which is the excess broadening due to phosphorus coupling as seen in the low- and high-temperature ^1H NMR.

only other transition-metal η^1-indenyl compound is nonfluxional.[10] The more rapid fluxional behavior of η^1-C_5H_5 compound **4** can best be explained by a 1,2 migration process. A similar 1,2 migration in the indenyl compound **7** would lead to intermediate **9** in which the aromaticity of the aryl ring is lost (Figure 3). In fact, 1,2 migration in the indenyl system may be retarded to such an extent that the observed fluxionality may be due to a direct 1,3 shift.

The reaction of PMe_3 (1.29 M) with $(\eta^5$-$C_9H_7)Re(CO)_3$, **6**, in CD_2Cl_2 at −65 °C was followed by ^1H NMR in an effort to detect a mono(phosphine) η^3-indenyl intermediate **8**. A rapid reaction was observed in which starting material **6** disappeared and a single new product, *fac*-$(\eta^1$-$C_9H_7)$-$Re(CO)_3(PMe_3)_2$, **7**, appeared. No evidence for η^3 intermediate **8** was seen; we estimate that 5–10% of intermediate **8** would have been easily detected. In the reaction of cyclopentadienyl complex **3** with PMe_3, the rate determining step was the formation of an η^3-C_5H_5 monophosphine intermediate which then reacted rapidly with PMe_3 to produce the η^1-C_5H_5 bis(phosphine) product **4**. We had hoped that the generation of the fully aromatic aryl ring in the mono(phosphine) η^3-indenyl intermediate **8** would increase our chances of observing an η^3 intermediate by accelerating the rate of the first phosphine addition step relative to the second phosphine addition step. However since no **8** was detected, apparently the second phosphine addition to **8** is still faster than the initial phosphine addition which generates **8**.

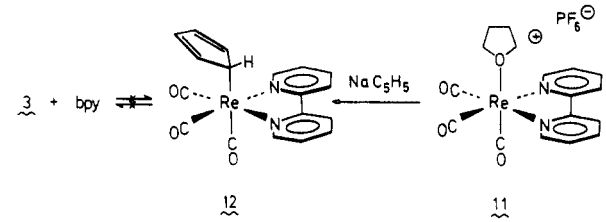
The rate of reaction of PMe_3 with **6** was measured by ^1H NMR at −65 °C. The pseudo-first-order rate constant was determined to be $(4.0 \pm 0.10) \times 10^{-4}$ s^{-1}; assuming a second-order rate law as observed for **4**, a second-order rate constant was calculated to be 3.3×10^{-4} M^{-1} s^{-1} at −65 °C; this corresponds to $\Delta G^{\ddagger} = 15$ kcal mol^{-1} at −65 °C. For comparison, the second-order rate constant for reaction of PMe_3 with η^5-C_5H_5 compound **4** at 88.3 °C was found to be about 1.8×10^{-5} M^{-1} s^{-1} which corresponds to $\Delta G^{\ddagger}$ = 29 kcal mol^{-1} at 88 °C. The difference in $\Delta G^{\ddagger}$ of about 14 kcal mol^{-1} between these two reactions is comparable to the $>10^8$ rate enhancement ($\Delta\Delta G^{\ddagger} > 10.7$ kcal mol^{-1}) reported by Basolo for related cyclopentadienyl- and indenylrhodium compounds.[6g-i] These large rate differences are undoubtedly related to the generation of a fully aromatic benzene ring in the proposed η^3-indenyl intermediate **8**.

The η^1-indenyl complex **7** is kinetically and thermodynamically a very stable system. When a solution of **7** was heated at 65 °C for 1 h in the probe of a Bruker WH-270 NMR spectrometer, no dissociation of PMe_3 was observed and no formation of substitution products was seen.

PBu_3 Adduct. Previously, we had unsuccessfully attempted to form η^1-C_5H_5–bis(tri-*n*-butylphosphine) adducts by reaction of PBu_3 either with $(\eta^5$-$C_5H_5)Re(CO)_3$, **3**, or with $(\eta^5$-$C_5H_5)Re(CO)(NO)CH_3$, **1**, both of which form stable bis(phosphine) adducts with the less hindered PMe_3. No reaction between **3** and PBu_3 was seen up to 100 °C. When **1** was heated at 90 °C with PBu_3, a second-order reaction occurred to give $(\eta^5$-$C_5H_5)Re(NO)(PBu_3)CH_3$ and $(\eta^5$-$C_5H_5)Re(NO)(PBu_3)COCH_3$; the reaction was suggested to proceed via an unobserved η^3-C_5H_5 mono(phosphine) intermediate.[3,4]

The enhanced stability of η^1-indenyl complex **7** encouraged us to study the reaction of PBu_3 with **6** in an effort to observe a more crowded bis(phosphine) η^1-indenyl complex. When PBu_3 was added to a slurry of **6** in hexane, an immediate reaction took place to produce a light yellow solution from which *fac*-$(\eta^1$-$C_9H_7)Re(CO)_3(PBu_3)_2$, **10**, was isolated in 87% yield. The structure of **10** was assigned on the basis of the similarity of its IR and ^1H and ^{31}P NMR to those of **7**. In particular, the low-temperature ^1H NMR of **10** has seven nonequivalent hydrogens, the low-temperature ^{31}P NMR has two resonances for the diastereotopic PBu_3 ligands, and the IR shows a characteristic three-band pattern expected for a facial isomer. As in the case of PMe_3 adduct **7**, the room-temperature ^1H and ^{31}P NMR provide evidence for a fluxional η^1-indenyl system. It is remarkable that the tendency of the indenyl system to assume an η^1 configuration is strong enough to allow two bulky PBu_3 ligands with cone angles of 132° to enter cis positions.[11]

2,2′-Bipyridyl Adduct. To see if nitrogen ligands could induce an η^5 to η^1 rearrangement, we heated $(\eta^5$-$C_5H_5)$-$Re(CO)_3$, **3**, with neat 2,2′-bipyridyl (bpy) at 80 °C but failed to observe any reaction. The fact that the desired η^1-C_5H_5–bpy adduct is a stable isolable compound was established by independent synthesis. Reaction of the known *fac*-$Re(CO)_3(bpy)Br$[12] with $AgPF_6$ in tetrahydrofuran led to precipitation of silver bromide and formation of the cationic THF adduct **11** which was isolated and characterized. Addition of NaC_5H_5 to a THF solution of **11** led to precipitation of orange *fac*-$(\eta^1$-$C_5H_5)Re(CO)_3$-(bpy), **12**, in 95% yield.[13] η^1-C_5H_5 complex **12** decomposes slowly in acetone at room temperature over several days. No $(\eta^5$-$C_5H_5)Re(CO)_3$, **3**, is produced upon decomposition.



With the more reactive indenyl complex **6**, we observed a slow reaction at 54 °C with 1 equiv of bpy in benzene-d_6. The 1:1 adduct *fac*-$(\eta^1$-$C_9H_7)Re(CO)_3(bpy)$, **13**, formed in 88% yield and was isolated as a red solid. In the low-temperature ^1H NMR of **13**, the 15 chemically different protons give rise to at least 14 different multiplets between δ 4.4 and 8.7. In the room-temperature NMR, a fluxional process interconverts three pairs of protons on the indenyl ligand and four pairs of protons on the bpy ligand, and seven different multiplets are seen. As expected for the assigned facial configuration, the two halves of the bpy ligand are NMR nonequivalent at low temperature and equivalent at room temperature. A meridinal configuration would have led to two nonequivalent pyridyl rings at all temperatures. While **7** and **10** have three CO stretches in the IR, **13** has only two bands, a sharp band at 2004 cm^{-1} and a broad band at 1900 cm^{-1}.

We suggest that the failure of bpy to react with $(\eta^5$-$C_5H_5)Re(CO)_3$, **3**, is a kinetic problem. The ability of bpy to induce an η^5 to η^1 rearrangement is much less than that of PMe_3 or PBu_3. For example $(\eta^5$-$C_9H_7)Re(CO)_3$, **6**, reacts with PMe_3 rapidly at −65 °C but only reacts slowly with bpy at +54 °C. We know that independently synthesized *fac*-$(\eta^1$-$C_5H_5)Re(CO)_3(bpy)$, **12**, decomposes slowly in solution at room temperature and that solutions of $(\eta^5$-$C_5H_5)Re(CO)_3$, **3**, are stable at 80 °C. Therefore, the rate

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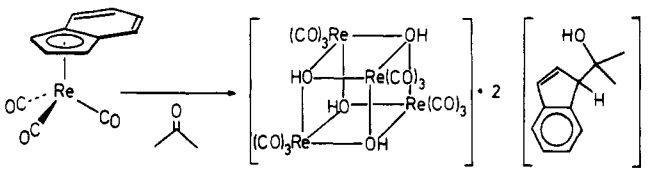
(12) Horn, E.; Snow, M. R. *Aust. J. Chem.* **1980**, *33*, 2369–2376.

(13) At 25 °C, $BrRe(CO)_3(bpy)$ reacts slowly (approximately 1.5 days) with NaC_5H_5 in THF to give **12**; however, decomposition of **12** begins to occur before reaction is complete.

of formation of *fac*-(η^1-C_5H_5)Re(CO)$_3$(bpy), **12**, must be extremely slow. We have no information regarding the relative thermodynamic stability of **3** and **12** since we have never been able to observe their interconversion.

Rhenium Tetramer Formation. Since the η^5-indenyl system underwent η^5 to η^1 rearrangement with both PMe_3 (cone angle 118°) and the bulkier PBu_3 (cone angle 132°), we attempted to look for a bis(phosphine) η^1-indenyl product in the reaction with the extremely bulky tricyclohexylphosphine ligand (PCy_3, cone angle 170°). When a solution of (η^5-C_9H_7)Re(CO)$_3$, **6**, was heated with PCy_3 in acetone-d_6 for 3 days at 55 °C, starting material disappeared and a new product appeared. The new material had NMR resonances for a nonfluxional indenyl system even at room temperature. No change in the PCy_3 ^1H NMR resonances was seen, and we suspected that it might not be involved in the reaction.

Indeed, when **6** was heated in acetone for 2 weeks at 88 °C, a new compound, [Re(CO)$_3$OH]$_4$·2[$C_9H_7C(CH_3)_2OH$], **14**, was isolated. The reaction is accelerated by added

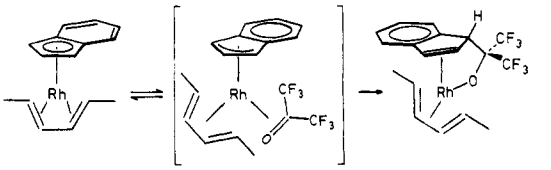


6 **14**

water. The structure of **14** consists of a cubic array with four Re(CO)$_3$ and four OH units at the vertices; in addition, two molecules of 1-[(1-hydroxy-1-methyl)ethyl]indene are associated with each rhenium tetramer. The ^1H NMR of this material had all the indenyl resonances seen in the product formed in the presence of PCy_3. In addition, the spectrum has singlets at δ 1.29 and 0.93 for the diastereotopic methyl groups α to the indenyl alcohol, at δ 6.60 for the μ_3-OH of the rhenium tetramer, and at δ 3.91 for the hydroxy group of the indenyl alcohol; these resonances were not in the PCy_3 reaction that was run in deuterated acetone. The 2:1 nature of the adduct was established by elemental analysis and by integration of ^1H NMR hydroxyl resonances, both of which underwent slow exchange with D_2O.

The known [Re(CO)$_3$OH]$_4$, **15**,[14] and the known indenyl alcohol **16**[15] were synthesized as described previously. When a 1:5 molar ratio of **15** and **16** were dissolved in acetone, the same 1:2 adduct **14** was formed as shown by comparison of melting point behavior and ^1H NMR and IR spectra. In acetone-d_6, 1:2 adduct **14** apparently dissociates since its ^{13}C and ^1H NMR spectra are the superposition of the NMR spectra of the isolated components **15** and **16**. In THF, the IR spectrum of **14** is identical with that of [Re(CO)$_3$OH]$_4$·4THF in THF; this provides further evidence for the dissociation of 1:2 adduct **14** in solution.

Green has observed a related reaction of (η^5-indenyl)rhodium complex **17** with hexafluoroacetone that produces the indenyl–alcoholate complex **18** shown below.[16] To explain the stereochemistry of the product in which the oxygen and alkene ligands are both bonded to rhodium, Green proposed that carbon–carbon bond formation might occur via intermediate **19** with an η^3-indenyl ligand and a coordinated ketone. The reaction reported here may occur by a similar mechanism.



17 **19** **18**

Experimental Section

General Data. Solvents were distilled from sodium and benzophenone (C_6D_6, hexane), CaH_2 (CD_2Cl_2), or B_2O_3 (acetone) prior to use. All reactions were run under dry nitrogen, except where indicated. ^1H NMR spectra were recorded on a Bruker WH-270 (270 MHz) or IBM WP200 (200 MHz) spectrometer; ^{13}C NMR (50.10 MHz) and ^{31}P NMR (80.76 MHz) were recorded on a JEOL FX-200 spectrometer. ^{31}P chemical shifts are referenced in parts per million from 85% H_3PO_4; upfield shifts are recorded as negative. Infrared spectra were recorded on a Beckman 4230 infrared spectrometer. Mass spectra were obtained on a AEI-MS-902 mass spectrometer. Melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Elemental analyses were performed by Schwarzkopf Microanalytical Labs.

***fac*-(η^1-C_9H_7)Re(CO)$_3$(PMe_3)$_2$, 7.** PMe_3 (1.03 mmol, 0.17 M) was condensed into a slurry of (η^5-C_9H_7)Re(CO)$_3$, **6** (132 mg, 0.34 mmol), in 6 mL of hexane at −78 °C. The slurry was stirred for 1 h at $J_{PH+P'H}$ °C, concentrated to 2 mL, and filtered to give **7** (174 mg, 95%) as a white solid: mp (sealed capillary) 146–162 °C dec; ^1H NMR (acetone-d_6, −68 °C) δ 7.36 (m, 2 H), 6.99 (m, 1 H), 6.94 (m, 1 H), 6.84 (m, 1 H), 6.31 (d, J = 4.6 Hz, 1 H), 3.81 (m, 1 H), 1.86 (d, J_{PH} = 8.3 Hz, 9 H), 1.69 (d, J = 8.5 Hz, 9 H); ^1H NMR (acetone-d_6, 40 °C) δ 7.39 (m, 2 H), 6.99 (m, 1 H), 6.90 (m, 2 H), 5.16 (br, 2 H), 1.72 (three lines, $J_{PH+P'H}$ = 8.2 Hz, 18 H); ^1H NMR (CD_2Cl_2, −68 °C) δ 7.40 (m, 2 H), 6.96 (m, 3 H) 6.37 (m, 1 H), 3.81 (m, 1 H), 1.74 (d, J = 8.1 Hz, 9 H), 1.57 (d, J = 8.1 Hz, 9 H); ^{13}C NMR (acetone-d_6, −70 °C) δ 194.1 and 193.0 (two broad resonances separated by 50 Hz assigned either as two broad singlets or two overlapping doublets due to chemically nonequivalent CO's trans to PMe_3), 190.9 (CO trans to C_9H_7), 157.5 (C8, C9), 147.5 (d, J = 158 Hz), 120.9 (d, J = 158 Hz), 119.8 (d, J = 158 Hz), 113.2 (d, J = 167 Hz), 29.7 (d, J = 139 Hz), 18.3 (qt, J = 130, 32 Hz, PMe_3); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −70 °C) δ −43.1 (d, J = 31 Hz), −46.6 (d, J = 31 Hz); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 0.09 M Cr(acac)$_3$, 27 °C) δ −44.5; IR (CH_2Cl_2) 2021 (vs), 1936 (s), 1894 (s) cm^{-1}.

Anal. Calcd for $C_{18}H_{25}O_3P_2Re$: C, 40.22; H, 4.69. Found: C, 40.48; H, 4.88. Exact mass calcd for $^{187}ReC_{18}H_{25}O_3P_2$ 538.0836, found 538.0840.

Kinetics for Formation of 7. PMe_3 (0.34 mmol, 1.29 M) was condensed into an NMR tube containing a −76 °C CD_2Cl_2 solution of **6** (0.029 mmol, 0.112 M) and 1,4-bis(trimethylsilyl)benzene (0.02 M) as internal standard. The tube was sealed, shaken at −76 °C, and placed in an NMR probe precooled to −65 °C. The initial ^1H NMR spectrum showed 15% reaction, and the reaction was monitored ten times over 39 min until 49% reaction had occurred. The observed pseudo-first-order rate constant for disappearance of **6** was found to be (4.0 ± 0.1) × 10^{-4} s^{-1}. The second-order rate constant was calculated to be 3.3 × 10^{-4} M^{-1} s^{-1} using 1.22 M as the average PMe_3 concentration. This corresponds to $\Delta G^{\ddagger}$ = 15 kcal mol^{-1} at −65 °C.

***fac*-(η^1-C_9H_7)Re(CO)$_3$(PBu_3)$_2$, 10.** A slurry of **6** (136 mg, 0.35 mmol) and PBu_3 (142 mg, 0.70 mmol) in hexane was stirred for 1 h at 25 °C. The resulting yellow solution was evaporated to give **10** (241 mg, 0.31 mmol, 87% yield) as a viscous oil contaminated by about 5% excess PBu_3: ^1H NMR (CD_2Cl_2, −70 °C) δ 7.47 (m, 2 H), 7.05 (m, 2 H), 6.93 (m, 1 H), 6.46 (m, 1 H), 4.18 (m, 1 H), 2.00 (m, 12 H), 1.43 (m, 24 H), 0.97 (m, 18 H); ^1H NMR (CD_2Cl_2, 27 °C) δ 7.29 (m, 2 H), 6.82 (m, 2 H), 6.75 (m, 1 H), 5.32 (br, 2 H), 1.76 (br), 1.27 (br), 0.78 (br) (total of 54 H); ^{13}C NMR (CD_2Cl_2, −68 °C) δ 194.0 and 192.9 (two broad resonances separated by 50 Hz assigned either as two broad singlets or two

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overlapping doublets due to chemically nonequivalent CO's trans to PBu_3), 191.9 (CO trans to C_9H_7), 157.2, 148 (d, J = 158 Hz), 139.6, 121.5 (d, J = 149 Hz), 120.0 (d, J = 158 Hz), 113.9 (d, J = 162 Hz), 28.6 (downfield portion of doublet of C_1; upfield portion partially obscurred by multiplet at δ 26.0), 26.0 (m), 24.3 (m), 13.8 (q, J = 125 Hz); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −70 °C) δ −23.7 (d, J = 27 Hz), −26.4 (d, J = 27 Hz); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 23 °C) δ −25.0 (br); IR (CH_2Cl_2) 2012 (vs), 1921 (s), 1884 (s) cm^{-1}.

Exact mass calcd for $^{187}ReC_{36}H_{61}O_3P_2$ 790.3641, found 790.3624.

[*fac*-$(C_4H_8O)Re(CO)_3(bpy)]^+ PF_6^-$, 11. $AgPF_6$ (306 mg, 1.14 mmol) was added to a THF solution of *fac*-$Re(CO)_3(Br)(bpy)$[12] (750 mg, 1.14 mmol, 0.02 M) at 25 °C. After 1 h the solution was filtered through Celite to remove the AgBr precipitate and the solvent evaporated under vacuum to give **11** as a yellow solid (730 mg, 1.11 mmol, 97%): ^1H NMR (CD_2Cl_2) δ 9.10 (m, 2 H), 8.55 (m, 2 H), 8.38 (m, 2 H) 7.78 (m, 2 H), 3.53 (m, 4 H), 1.78 (m, 4 H); IR (CH_2Cl_2) 2034 (s), 1932 (vs) cm^{-1}.

Anal. Calcd for $C_{17}H_{16}O_4N_2PF_6Re$: C, 31.68; H, 2.66; N, 4.35. Found: C, 31.48; H, 2.47; N, 4.34.

***fac*-$(\eta^1$-$C_5H_5)Re(CO)_3(bpy)$, 12.** Addition of NaC_5H_5·THF (76 mg, 0.455 mmol) to a THF (25 mL) solution of **11** (300 mg, 0.455 mmol, 0.018 M) led to precipitation of orange **12** (212 mg, 0.43 mmol, 95%): mp (sealed capillary) 180–181.5 °C dec; ^1H NMR (acetone-d_6) δ 8.88 (m, 2 H), 8.57 (m, 2 H) 8.18 (m, 2 H), 7.68 (m, 2 H), 5.24 (s, 5 H); $^{13}C\{^1H\}$ NMR (acetone-d_6, 0.09 M $Cr(acac)_3$) δ 155.9, 153.6, 139.5, 127.8, 124.6, 111.2 (C_5H_5); IR (CH_2Cl_2) 2010 (vs), 1904 (s), 1890 (shoulder) cm^{-1}.

Anal. Calcd for $C_{18}H_{13}N_2O_3Re$: C, 43.99; H, 2.66; N, 5.70. Found: C, 43.83; H, 2.59; N, 5.68.

***fac*-$(\eta^1$-$C_9H_7)Re(CO)_3(bpy)$, 13.** An NMR tube containing a solution of **6** (67.1 mg, 0.174 mmol) and 2,2′-bipyridyl (27.2 mg, 0.174 mmol) in benzene-d_6 (0.35 mL) was heated at 54.0 ± 0.2 °C and periodically monitored by ^1H NMR. After 60 h, **6** and bpy were 95% converted to a new compound, **13**, with resonances at δ 8.11 (m, 2 H), 6.82 (m, 1 H), 6.70 (m, 2 H), 6.56 (br, 4 H), 6.48 (m, 2 H), 6.14 (m, 2 H), and 5.3 (br, 2 H). When the NMR tube was opened, **13** spontaneously crystallized. Hexane was added, and red microcrystalline **13** [83 mg, 88%, mp (sealed capillary) 172–178 °C dec] was isolated by filtration. Recrystallization of **13** from THF/hexane gave **13** as an orange powder: ^1H NMR (CD_2Cl_2, −67 °C) δ 8.73 (d, J = 5.2 Hz, 1 H), 8.16 (d, J = 5.0 Hz, 1 H), 7.84 (m, 1 H), 7.75 (m, 1 H), 7.67 (m, 1 H), 7.38 (d, J = 8.1 Hz, 1 H), 7.22 (m, 2 H), 6.51 (m) and 6.47 (m) (2 H total), 6.67 (dd, J = 4.5, 1.6 Hz, 1 H), 6.26 (m, 1 H), 5.86 (d, J = 7.5 Hz, 1 H), 5.78 (d, J = 4.5 Hz, 1 H), 4.43 (d, J = 1.6 Hz, 1 H); ^1H NMR (CD_2Cl_2, 30 °C) δ 8.56 (d, J = 5.3 Hz, 2 H), 7.76 (m, 2 H), 7.66 (d, J = 8.0 Hz, 2 H), 7.21 (m, 24 H), 6.59 (m, 1 H), 6.46 (br, 4 H), 5.15 (br, 2 H); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, −71 °C) δ 153.7, 151.6, 150.2, 147.9, 141.2, 138.9, 136.8, 136.5, 125.5, 125.2, 122.6, 120.2, 119.3, 119.0, 118.4, 118.2, 112.3, 105.3, 42.1, only one weak resonance at δ 201.5 was seen for the CO's; IR (CH_2Cl_2) 2004 (vs), 1900 (s, br) cm^{-1}.

Anal. Calcd for $C_{22}H_{15}O_3N_2Re$: C, 48.79; H, 2.79; N, 5.17. Found: C, 48.79; H, 2.87; N, 5.37.

Attempted Reaction of 6 with PCy_3. An NMR tube containing a solution of **6** (9.5 mg, 0.025 mmol) and PCy_3 (14 mg, 0.05 mmol) in 0.35 mL of acetone-d_6 was heated at 55 °C for 3 days and monitored by NMR. After 3 days, the resonances due to **6** were replaced by a new set of resonances at δ 7.73 (m, 1 H), 7.32 (m, 1 H), 7.21 (m, 1 H), 7.15 (m, 1 H), 6.71 (ddd, J = 6, 2, 0.7 Hz, 1 H), 6.52 (dd, J = 6, 2 Hz, 1 H), and 3.57 (m, 1 H). No change was observed in the resonances due to PCy_3.

$[Re(CO)_3OH]_4$·2[$C_9H_7C(CH_3)_2OH$], 14, from 6 and Acetone. A sealed tube containing a solution of **6** (275.8 mg, 0.716 mmol, 0.26 M) and 2.8 mL of acetone was heated at 88 °C for 14 days. Evaporation of volatiles and trituration of the oily residue with 1:5 CH_2Cl_2/hexane (3 mL) led to formation of a white solid **14** (208 mg, 0.139 mmol, 77%): mp (sealed capillary) 195–197 °C dec; ^1H NMR (acetone-d_6) δ 7.73 (m, 1 H), 7.32 (m, 1 H), 7.21 (m, 1 H), 7.15 (m, 1 H), 6.84 (ddd, J = 5.7, 2.0, 0.7 Hz, 1 H) 6.60 (s, 2 H), 6.52 (dd, J = 5.6, 1.9 Hz, 1 H), 3.57 (m, 1 H), 3.91 (br, 1 H), 1.29 (s, 3 H), 0.93 (s, 3 H); $^{13}C\{^1H\}$ NMR (THF-d_8) δ 197.3, 146.2, 146.0, 137.7, 132.6, 127.0, 125.9, 125.0, 121.2, 72.4, 63.5, 29.7, 25.6; IR (THF) 3426 (br), 2027 (s), 1927 (vs) cm^{-1}.

Anal. Calcd for $C_{36}H_{32}O_{18}Re_4$: C, 28.88; H, 2.15. Found: C, 28.48; H, 2.10.

In a similar reaction run in H_2O/acetone (15:85), **6** was converted to **14** in 90% isolated yield after only 1 day.

$[Re(CO)_3OH]_4$·2[$C_9H_7C(CH_3)_2OH$], 14, from $[Re(CO)_3OH]_4$, 15, and $C_9H_7C(CH_3)_2OH$, 16. A solution of $[Re(CO)_3OH]_4$, **15**,[13] (204 mg, 0.18 mmol, 0.045 M) and $C_9H_7C(CH_3)_2OH$[14] (154 mg, 0.88 mmol, 0.22 M) in 4 mL of acetone was stirred at 25 °C for 30 min. Workup as above gave **14** (190 mg, 0.126 mmol, 70% yield) which was identified by IR, NMR, and melting point.

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Registry No. **6**, 33308-86-0; **7**, 93757-33-6; **10**, 93757-34-7; **11**, 93757-36-9; **12**, 93757-37-0; **13**, 93757-38-1; **14**, 93757-39-2; **14**-d_7, 93757-40-5; **15**, 56553-73-2; $C_9H_7C(CH_3)_2OH$, 20440-84-0; *fac*-$Re(CO)_3(Br)(bpy)$, 40231-87-6; NaC_5H_5·THF, 4984-82-1; acetone, 67-64-1; acetone-d_6, 666-52-4.