versible. At temperatures above 10 °C the broad resonances slowly disappeared, giving rise to a complex NMR spectrum containing several broad resonances.

Reaction of DMA with the (TBA)Ni(TPP)₂ Complexes. DMA (0.1 mmol) was added to a solution containing 0.05 mmol of tris(triphenylphosphine)nickel(0) and 0.1 mmol of TBA at <−60 °C (see preceding experimental). The NMR spectrum of the resulting solution showed the presence of free TBA (>95%) and the absence of free DMA. At temperatures above −20 °C the peaks of **1** appeared.

Reaction of Cyanoallene (CYA) with (TPP)₃Ni. In a rubber septum stoppered, 100-mL, round-bottom flask filled with argon was placed 3.0 mmol of (TPP)₃Ni in 25 mL of THF. The solution was cooled to −30 °C, and 0.39 g (6.0 mmol) of CYA was slowly added. The reaction mixture initially turned green in color and then rapidly turned red-orange in color. The reaction mixture was brought to 20 °C and stirred for 0.5 h. The volatiles were removed on a vacuum line, and the THF was removed by fractional distillation. No residue derived from CYA was present (by NMR).

The residue remaining after the removal of the volatiles was extracted with refluxing hexane. The hexane extract was filtered, and the hexane was removed under reduced pressure. The NMR spectrum of the residue showed only the presence of **37** in very low yield along with an extensive amount of TPP.

Carbonylation of the Cyanoallene–(TPP)₃Ni Reaction Mixture. In a rubber septum stoppered, 100-mL, round-bottom flask filled with argon was placed 3.0 mmol of (TPP)₃Ni in 25 mL of THF. The contents of the flask were cooled to −30 °C, and 0.39 g (6 mmol) of CYA was added. The reaction mixture was stirred for 0.5 h and brought to 20 °C. Carbon monoxide was bubbled through the solution (via a syringe needle) for 3 h. The volatiles were then removed on a vacuum line. Analysis of the volatile fraction by NMR showed no CYA-derived product. The residue was extracted with five 50-mL portions of refluxing ether. The extract was filtered and the ether was removed under reduced pressure, giving 0.7 g of a viscous residue. The residue was triturated with 3 mL of ether, and the white insoluble material [(TPP)₂Ni(CO)₂] was removed by filtration. The ether was evaporated, leaving 0.20 g of material which was chromatographed on a Chromatron with a 2 mm thick silica gel plate by eluting with hexane–methylene chloride mixtures.

Fraction 1 (Mixture of Two Trimers 39 and 40 or 41, 1.2% and 0.8%). **39**: NMR (CDCl₃) δ 2.91 (AA'BB' m, 4 H), 3.41 (br s, 2 H), 5.36 (br s, 1 H), 5.48 (s, 1 H), and 6.75 (s, 1 H); UV (of mixture, in 95% ethanol) λ_max 300 nm with shoulders at 288 and 313 nm; MS (of mixture), M⁺ exact mass calcd for C₁₂H₉N₃ 195.079, found 195.080. **40 or 41**: NMR (CDCl₃) δ 2.85 (m, 4 H), 3.45 (br s, 2 H), 5.46 (br s, 1 H), 5.50 (br s, 1 H), and 7.08 (br s, 1 H).

Fractions 2 and 3 contained only TPP.

Fraction 4 (36, 0.5%): NMR (CDCl₃) δ 3.05 (AA'BB' m, 4 H), 5.33 (br t, *J* = 2.12 Hz, 1 H), and 6.19 (br t, *J* = 2.65 Hz, 1 H); UV (95% ethanol) λ_max 280 nm with shoulders at 270 and 294 nm; MS, M⁺ *m/e* 130.

Fraction 5 (37, 6.5%): NMR (CDCl₃) 3.03 (t, *J* = 1.12 Hz, 4 H) and 5.62 (pent, 2 H); UV (95% ethanol) λ_max 283 nm with shoulders at 273 and 296 nm; MS, exact mass calcd for C₈H₆N₂ 130.053, found 130.053.

After elution with methylene chloride the silica gel plate was washed with methanol, giving material whose NMR spectrum was extremely complex showing many peaks in the δ 1.0–4.5 region.

Low-Temperature NMR Studies of the Reaction of CYA with (TPP)₃Ni. To 0.05 mmol of (TPP)₃Ni in 0.7 mL of THF-*d₈* at −70 °C contained in an NMR tube equipped with a screw cap and septum was added 0.10 mmol of CYA. The NMR spectrum recorded immediately showed only extremely broad resonances (including those of THF-*dₙ*). On slowly raising the temperature to 20 °C the peaks still remained quite broad. No peaks were evident in the vinyl hydrogen region.

Supplementary Material Available: Tables of positional parameters, calculated hydrogen atom positions, and temperature factor positions (3 pages). Ordering information is given on any current masthead page.

Synthesis and Reactions of a Cyclopentadienylidene Ketene Complex

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Abstract: (η¹-C₅H₅)Re(NO)(CH₃)(CO)(PMe₃)₂ (**5**) reacts with high concentrations of PMe₃ at 72 °C to give the cyclopentadienylidene ketene complex (PMe₃)₃(NO)ReC(C₅H₄)O (**8**) and methane. **8** reacts with acetone to give (PMe₃)₃-(NO)ReC(C₅H₄)OC(CH₃)₂O (**9**). **8** also reacts with HCl to give the enol complex (PMe₃)₃(NO)(Cl)ReC(C₅H₄)OH (**11**). Reaction of **5** with carbon monoxide gives the cyclopentadienylidene–ester bridged bimetallic complex **13**. (η¹-C₅H₅)Re-(NO)(CO)(H)(PMe₃)₂ (**15**) reacts with PMe₃ to give the very electron-rich complex (PMe₃)₃Re(NO)(CO) and cyclopentadiene.

The accessibility of open coordination sites at a metal is of prime importance in the design of catalytic systems. Exploitation of cyclopentadienyl ring slippage reactions (η⁵-C₅H₅ ⇌ η³-C₅H₅ ⇌ η¹-C₅H₅) as a method of obtaining open coordination sites on a metal catalyst will depend on the chemical reactivity of the η¹-C₅H₅ ligand. To date, the only well-characterized reactions of the η¹-C₅H₅ ligand are the formation of Diels–Alder adducts with dienophiles,[1] the conversion of η¹-C₅H₅ complexes to η⁵-C₅H₅ complexes,[2] and our recently discovered ionization of an η¹-C₅H₅ ligand.[9] Monohaptocyclopentadienyl complexes have been postulated as intermediates in a number of other reactions, such

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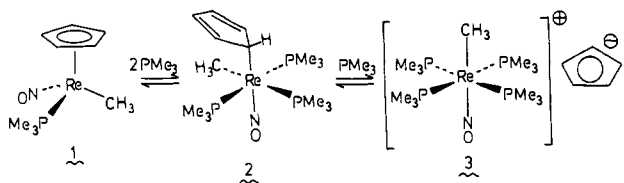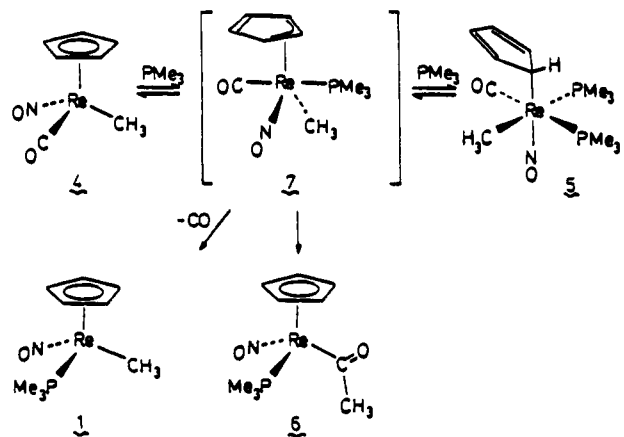
(7) Brintzinger, H. H.; Bercaw, J. E. *J. Am. Chem. Soc.* **1970**, *92*, 6182–6185.

as deuterium incorporation into η^5-C$_5$H$_5$ ligands,[3] intermolecular exchange of η^5-C$_5$H$_5$ ligands,[4] complete loss of η^5-C$_5$H$_5$ ligands,[5] racemization of chiral complexes,[6] and the conversion of an η^5-C$_5$H$_5$ mononuclear complex into a C$_5$H$_4$C$_5$H$_4$ bridged bimetallic complex[7] and as a means of obtaining open coordination sites for a variety of other reactions involving η^5-C$_5$H$_5$ metal complexes.[8]

We have recently reported that (η^5-C$_5$H$_5$)Re(NO)(CH$_3$)(PMe$_3$) (1) and PMe$_3$ reversibly form (η^1-C$_5$H$_5$)Re(NO)(CH$_3$)(PMe$_3$)$_3$ (2) in high yield.[9] When 2 is heated in the presence of excess PMe$_3$, reversible ionization of the η^1-C$_5$H$_5$ unit occurs to give [Re(NO)(CH$_3$)(PMe$_3$)$_4$]$^+$[C$_5$H$_5$]$^-$ (3), in good yield.

(η^5-C$_5$H$_5$)Re(NO)(CH$_3$)(CO) (4) reacts reversibly with 2 equiv of PMe$_3$ at 22 °C to give (η^1-C$_5$H$_5$)Re(NO)(CH$_3$)(CO)(PMe$_3$)$_2$ (5) in high yield.[2b] When a solution containing an equilibrium mixture of 4 and 5 is heated to 90 °C a 4:1 mixture of (η^5-C$_5$H$_5$)Re(NO)(CH$_3$)(PMe$_3$) (1) and (η^5-C$_5$H$_5$)Re(CO)(COCH$_3$)(PMe$_3$) (6) results. The formation of 1, 5, and 6 is believed to proceed via a common η^3-C$_5$H$_5$ mono(phosphine) intermediate 7.
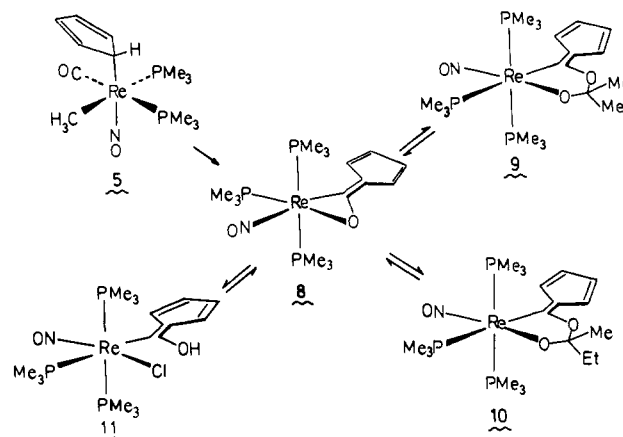

Here we report the discovery of yet another reaction path for η^1-C$_5$H$_5$ transition-metal complexes: the conversion of an η^1-cyclopentadienyl complex, 5, to a cyclopentadienylidene ketene complex, 8.[10] In addition, we have found that compound 5 reacts with carbon monoxide to give the cyclopentadienylidene–ester bridged bimetallic complex 13 which we have characterized by X-ray crystallography. In an attempt to prepare ketene complex 8 from (η^1-C$_5$H$_5$)Re(NO)(CO)(H)(PMe$_3$)$_2$ (15), and PMe$_3$, we observed reductive elimination of cyclopentadiene and formation of the electron-rich complex (PMe$_3$)$_3$Re(NO)(CO) (16).

Results

Synthesis of Ketene Complex 8. A toluene solution of (η^5-C$_5$H$_5$)Re(NO)(CH$_3$)(CO) (4) and PMe$_3$ (2.9 M) was heated at 72 °C for 17 h; ketene complex 8 was subsequently isolated in 28% yield from the reaction mixture. In addition, a 44% yield of methane was measured in a Toepler pump experiment. The structure of 8 was established by NMR, IR, and elemental analysis. The ^{1}H NMR of 8 in benzene-d_6 consists of a three-line

pattern at δ 1.05 ($J_{PH} + J_{P'H} = 7$ Hz, 18 H), assigned to two equivalent trans PMe$_3$ ligands and a doublet at 1.09 ($J_{PH} = 8.5$ Hz, 9 H) assigned to a unique PMe$_3$ ligand. Four multiplets (1 H each) are observed in the δ 6.89–7.30 range and are attributed to four nonequivalent protons on the cyclopentadiene ring. The observation of four different cyclopentadiene protons allows us to exclude a more symmetric η^2-cyclopentadienylidene-*C,C* ketene structure for which only two different cyclopentadiene resonances would be observed. The IR spectrum of 8 (THF) has a band at 1621 cm^{-1}, assigned to a linear nitrosyl ligand, and a band at 1550 cm^{-1} assigned to either the C—O or C=C stretch of the ketene ligand. For comparison, the η^2-ketene-*C,O* complex [(η^5-C$_5$H$_5$)$_2$TiOC=CH$_2$]$_n$ has a band at 1610 cm^{-1}[11] while the η^2-C,C complex (η^5-C$_5$H$_5$)Mn(CO)$_2$(Ph$_2$CC=O) has a band at 1787 cm^{-1}.[12] A cyclopentadienylidene rhenium structure for 8 is excluded on the basis of three observations. First, the mass spectrum of 8 shows a peak match for C$_{15}$H$_{31}$NO$_2$P$_3$Re, indicating incorporation of the carbon monoxide ligand in some form. Second, the infrared spectrum of 8 indicates the absence of a terminal carbon monoxide ligand. Third, the ^{13}C{^{1}H} NMR of 8 has a resonance of δ 214.1 ($\nu_{1/2} = 29$ Hz) which is similar to that seen for the ketene carbons in other transition-metal ketene complexes.[13] The unresolved P–C coupling for the δ 214.1 ^{13}C NMR resonance of 8 does not allow definitive placement of the unique PMe$_3$ ligand relative to the carbon bonded to ·nium.

For preparative purposes, 8 was best synthesized by photolysis of 4 in the presence of PMe$_3$. When a toluene solution of 4 and PMe$_3$ (4.05 M) was photolyzed at 366 nm for 5 days a 66% yield of methane and a 59% yield of 8 were isolated from the reaction

mixture. In a related experiment, the ^{1}H NMR spectrum of a benzene-d_6 solution of 4 and PMe$_3$ (2.9 M) indicated quantitative conversion of 4 to (η^1-C$_5$H$_5$)Re(NO)(CH$_3$)(CO)(PMe$_3$)$_2$ (5), which was stable at 32 °C in the dark. Photolysis of this solution at 366 nm for 80 h led to the formation of 8 in 67% yield. In addition, equal intensity multiplets at δ 6.44, 6.27, and 2.71 were observed and are assigned to cyclopentadiene (30%).

Reactions of 8 with Ketones. Ketene complex 8 undergoes a slow reversible reaction with ketone solvents at room temperature. When an acetone solution of 8 was stirred at 26 °C for 48 h, a 92% yield of acetone adduct 9 was isolated as a yellow solid. In the ^{1}H NMR spectrum (benzene-d_6) of 9, a three-line pattern at δ 1.19 ($J_{PH+P'H} = 6.8$ Hz), assigned to equivalent trans PMe$_3$ ligands, indicates that the plane of symmetry in 8 is also maintained in acetone adduct 9. A doublet at δ 1.02 ($J = 7.9$ Hz) is assigned to the unique PMe$_3$ ligand, and a singlet at δ 1.36 (6 H) is assigned to the *gem*-dimethyl protons derived from acetone. Multiplets at δ 7.36 (2 H), 6.96 (1 H), and 6.90 (1 H) are assigned

(8) For selected examples, see: Kalina, D. G.; Marks, T. J.; Wachter, W. A. *J. Am. Chem. Soc.* 1977, *99*, 3877–3878. Wegman, R. W.; Brown, T. L. *Organometallics* 1982, *1*, 47–52. Jones, W. D.; Feher, F. J. *Organometallics* 1983, *2*, 686–687.

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(10) A preliminary communication of portions of this work has appeared: Casey, C. P.; O'Connor, J. M. *J. Am. Chem. Soc.* 1983, *105*, 2919–2920.

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(13) The ketene carbon bonded to oxygen in [(η^5-C$_5$H$_5$)$_2$Ti(OC=CH$_2$)]$_2$ comes at δ 220[11] and in (η^5-C$_5$H$_5$)Mn(CO)$_2$(OC$_2$Ph$_2$) at δ 201.3.
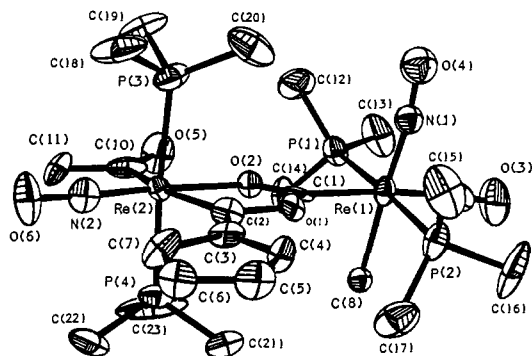
Figure 1. ORTEP of **13**.

to the four protons of the cyclopentadiene ring.

In the $^{13}C\{^1H\}$ NMR (CD$_2$Cl$_2$) of **9**, a doublet at δ 238.2 (J_{PC} = 55 Hz) is assigned to the carbon bonded to rhenium and establishes the trans geometry of the unique PMe$_3$ ligand and that carbon.
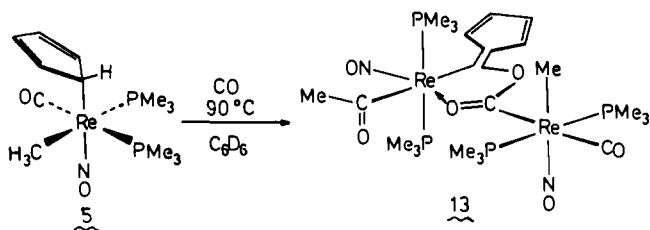
The formation of **9** from acetone was shown to be reversible by heating a 0.036 M benzene-d_6 solution of **9** at 80 °C for 4 h. Periodic observation by ^1H NMR indicated the clean conversion of **9** to **8** and free acetone with a half-life of ~60 min at 80 °C.

A related 2-butanone adduct, **10**, was isolated as a brown solid in 65% yield from a solution of **8** in 2-butanone after 2 days at 26 °C. Consistent with the structures assigned to **8** and **9**, the ^1H NMR (CD$_2$Cl$_2$) of **10** indicates the absence of a symmetry plane in **10**. The three PMe$_3$ ligands are nonequivalent leading to a pair of three-line patterns at δ 1.50 ($J_{PH+P'H}$ = 6.8 Hz) and 1.47 ($J_{PH+P'H}$ = 6.8 Hz) and a doublet at 1.61 (J_{PH} = 8.1 Hz).

Formation of (PMe$_3$)$_3$(NO)(Cl)ReC(C$_5$H$_4$)OH (11). In the hope of obtaining a (cyclopenta-2,4-dienyl)carbonylmetal complex we examined the reaction of **8** with HCl. Upon addition of 1 equiv of HCl gas to a −78 °C THF slurry of **8**, an immediate darkening of the yellow solution occurred. Workup of the resulting opaque yellow slurry gave **11** as a yellow solid in 86% yield. In the ^1H NMR (CD$_2$Cl$_2$) of **11**, a doublet at δ 9.13 (J_{PH} = 4.4 Hz, 1 H), which disappeared upon addition of D$_2$O, is assigned to a hydroxyl proton resonance. The low-field chemical shift of this signal is to be indicative of hydrogen bonding to the neighboring chlorine ligand. For comparison, the hydrogen-bonded hydroxyl proton of Re[C(OH)CH$_3$](CO)(Cl)(N$_2$)(PPh$_3$)$_2$ (**12**) was reported at δ 14.0 in the ^1H NMR.[14] The IR spectrum (THF) of **11** has a weak, broad band at 3346 cm^{-1} consistent with the presence of intramolecular OH···Cl hydrogen bonding.

Compound **11** rapidly reverted to **8** upon reaction with *n*-BuLi at −78 °C.

Formation of Bimetallic Complex 13. When a benzene solution of (η^1-C$_5$H$_5$)Re(NO)(CH$_3$)(CO)(PMe$_3$)$_2$ (**5**) was heated at 90 °C for 4 h under 1000 psi of carbon monoxide an 18% yield of a yellow-orange solid **13** was isolated by chromatography (silica

gel–Et$_2$O). The ^1H NMR of **13** in acetone-d_6 consisted of four multiplets (1 H each) between δ 6.92 and 6.06, similar to the patterns observed for **8–11**. In addition, three-line patterns at δ 1.86 ($J_{PH+P'H}$ = 8.4 Hz, 18 H) and 1.34 ($J_{PH+P'H}$ = 7.6 Hz, 18 H) indicated the presence of two sets of equivalent trans PMe$_3$ ligands. A three-proton singlet at δ 2.35 and a three-proton triplet at δ −0.69 (J_{PH} = 10.7 Hz) are assigned to the hydrogens of an
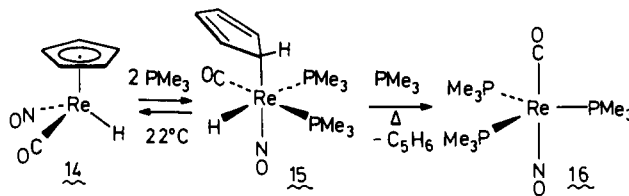
Table I. Selected Interatomic Distances (Å) and Angles (deg) for Molecule 1 of **13**[a]

atoms	distances	atoms	angles
Re(1)–C(1)	2.125 (7)	P(1)–Re(1)–P(2)	176.8 (2)
Re(1)–C(8)	2.239 (6)	P(2)–Re(1)–C(1)	91.7 (3)
Re(1)–C(9)	2.001 (8)	C(1)–Re(1)–C(9)	172.9 (7)
Re(2)–C(2)	2.108 (9)	C(1)–Re(1)–N(1)	88.0 (9)
Re(2)–C(10)	2.165 (7)	P(3)–Re(2)–P(4)	174.3 (2)
Re(2)–O(2)	2.165 (5)	P(3)–Re(2)–O(2)	87.9 (3)
C(1)–O(1)	1.390 (13)	P(3)–Re(2)–C(2)	91.1 (3)
C(1)–O(2)	1.234 (12)	P(4)–Re(2)–O(2)	86.5 (3)
O(1)–C(2)	1.424 (11)	P(4)–Re(2)–C(2)	88.4 (3)
C(2)–C(3)	1.368 (12)	O(2)–Re(2)–C(2)	73.2 (3)
C(3)–C(4)	1.455 (10)	O(2)–Re(2)–C(10)	85.0 (4)
C(3)–C(7)	1.459 (10)	O(2)–Re(2)–N(2)	176.3 (5)
C(4)–C(5)	1.331 (10)	C(2)–Re(2)–C(10)	158.0 (3)
C(5)–C(6)	1.427 (14)	C(2)–Re(2)–N(2)	103.5 (5)
C(6)–C(7)	1.331 (10)	Re(2)–C(2)–O(1)	114.0 (7)
		Re(2)–C(2)–C(3)	135.8 (6)
		O(1)–C(2)–C(3)	110.2 (7)
		C(2)–C(3)–C(4)	132.8 (7)
		C(2)–C(3)–C(7)	123.9 (6)

[a] The estimated standard deviation of the least significant digits are given in parentheses.

acetyl ligand and a methyl ligand, respectively. An IR band at 1986 cm^{-1} is assigned to a terminal carbonyl ligand, while bands at 1692 and 1650 cm^{-1} are assigned to two linear nitrosyl stretches. The structure of **13** was unambiguously determined by X-ray crystallographic analysis (Figure 1, Table I). Two independent molecules per unit cell were seen.

Formation of (PMe$_3$)$_3$Re(NO)(CO) (16) from (η^5-C$_5$H$_5$)Re-(NO)(CO)(H), (14). We have previously reported that the reaction of (η^5-C$_5$H$_5$)Re(NO)(CO)(H) (**14**) and PMe$_3$ at 25 °C forms (η^1-C$_5$H$_5$)Re(NO)(CO)(H)(PMe$_3$)$_2$ (**15**).[2b] Conceivably **15** could react with excess PMe$_3$ at elevated temperatures to give ketene complex **8** and H$_2$, by analogy with the reaction of **5** with PMe$_3$ which gave **8** and methane. However, when a THF solution of **14** (0.74 mmol, 0.09 M) and PMe$_3$ (4.32 mmol, 0.51 M) was heated at 80 °C for 15 min an 81% isolated yield of (PMe$_3$)$_3$Re(NO)(CO) (**16**) was obtained as a dark maroon solid.

In a separate ^1H NMR experiment, the initial formation of (η^1-C$_5$H$_5$)Re(NO)(CO)(H)(PMe$_3$)$_2$ (**15**) was observed at 25 °C. When this solution was heated at 50 °C for 20 min, **15** was quantitatively converted to **16** and an equimolar amount of cyclopentadiene. In the ^1H NMR of **16**, a broadened quartet at δ 1.35 is assigned to the three PMe$_3$ ligands. In the $^{13}C\{^1H\}$ NMR of **16**, a broad resonance at δ 23.5 is assigned to the carbons of the three PMe$_3$ ligands and a resonanance at δ 222.6 is assigned to the terminal CO ligand. The IR spectrum of this very electron-rich Re(−I) compound has bands at 1820 and 1560 cm^{-1} assigned to the terminal CO and NOr stretches, respectively. The related complex Re(CO)$_2$(NO)(PPh$_3$)$_2$ has IR bands at 1950, 1870, and 1620 cm^{-1}.[15]

Discussion

The unprecedented formation of cyclopentadienylidene ketene complex **8** from **4** is surprising in light of the extensive phosphine substitution chemistry previously observed for related η^5-C$_5$H$_5$ transition-metal alkyl complexes. Recently we reported that under conditions of low PMe$_3$ concentration the equilibrium mixture of **4** and **5** is converted to the η^5-C$_5$H$_5$ phosphine-substitution

(14) Chatt, J.; Leigh, G. J.; Pickett, C. J.; Stanley, D. R. *J. Organomet. Chem.* **1980**, *184*, C64–C66.
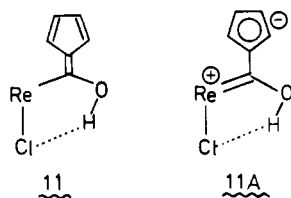
(15) LaMonica, G.; Freni, M.; Cenini, S. *J. Organomet. Chem.* **1974**, *71*, 57–64. Reed, C. A.; Roper, W. R. *J. Chem. Soc. A* **1970**, 3054–3059.

products, **1** and **6**, probably via an η^3-C_5H_5 mono(phosphine) intermediate **7**. It appears that the key to the formation of ketene complex **8** lies in the use of high PMe_3 concentration to drive the **4** + 2PMe_3 $\rightleftarrows$ **5** equilibrium to the side of η^1-C_5H_5 complex **5**. This, in effect, inhibits the reaction path leading to **1** and **6** and results in the previously unobserved conversion of an η^1-C_5H_5 ligand to a cyclopentadienylidene ketene ligand.
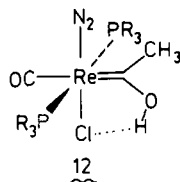
Other transition-metal ketene complexes have been prepared by direct reaction of ketenes with coordinatively unsaturated metal complexes,[16] by carbonylation of metal alkylidene complexes,[17] and by deprotonation of metal acyl complexes.[11]

The mechanism for formation of ketene complex **8** is necessarily complex due to the large number of bonds that must be broken or formed in the process. Formally, **8** is the result of carbon monoxide insertion into an (η^1-C_5H_5)–Re bond followed by loss of a cyclopentadiene hydrogen. Although such an insertion process is known for many metal alkyl complexes, it has not been reported for η^1-C_5H_5 metal complexes. Indeed, no (cyclopenta-2,4-dienyl)carbonylmetal complexes have been reported.
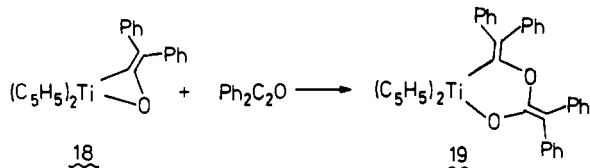
We attempted to prepare a (cyclopenta-2,4-dienyl)carbonyl complex by reaction of HCl with **8**. However, spectroscopic studies indicate that the product is the enol form, **11**, of the desired

11   **11A**

(cyclopenta-2,4-dienyl)carbonyl complex. In contrast to enol **11**, both formylcyclopentadiene and acetylcyclopentadiene have been observed only as their keto tautomers **17**.[18] We attribute the preference of **11** for the enol form to hydrogen bonding of the hydroxyl proton to the neighboring chlorine ligand. Resonance structure **11A**, which has a Re=C double bond and a cyclopentadienyl anion, may also help to account for the stability of the enol form of **11**.

12

The reactions of ketene complex **8** with ketones to give **9** and **10** is analogous to Floriani's report of a reversible addition reaction of diphenylketene and $[(\eta^5$-$C_5H_5)_2Ti(Ph_2C_2O)]_2$ (**18**), to give the ring-expanded product **19**.[16] Floriani suggested that formation

of **19** is the result of insertion of the C=O bond of the ketene into the Ti–O bond of **18**. The alternative process, an insertion into the Ti–C bond of **18**, would also lead to **19**.[19] In the reaction

of **8** with ketones, the carbonyl bond is clearly inserting into the Re–O bond of **8**.

The reaction of η^1-C_5H_5 bis(phosphine) complex **5** with carbon monoxide to give bimetallic complex **13** is the formal result of insertion of the ReC≡O bond of a cationic complex, [Re-$(CO)_2(PMe_3)_2(NO)(CH_3)]^+$ (**A**), into the Re–O bond of an an-

A   **B**

ionic cyclopentadienylidene ketene complex, [Re(COCH₃)-(NO)(PMe₃)₂(CC₅H₄O)]⁻ (**B**). This insertion would be analogous to the reaction of ketene complex **8** with ketones. The formation of an intermediate species similar to **A** has precedence in the PMe_3-induced loss of an η^1-C_5H_5 ligand from **1** to give **3**. A surprising feature of compound **13** is that neither rhenium has lost its methyl ligand in the form of methane (as was the case in the formation of **8**). The observation of cyclopentadiene in the reaction mixture may indicate that the hydrogen lost from one C_5H_5 unit has combined with the C_5H_5 ligand lost from the other rhenium.

It was anticipated that $(\eta^5$-$C_5H_5)Re(NO)(CO)(H)$ (**14**) might also react with PMe_3 to form ketene complex **8** and hydrogen. However, upon heating **14** and PMe_3 a rapid reaction to give $(PMe_3)_3Re(NO)(CO)$ (**16**) and C_5H_6 occurred. Apparently the reductive elimination of the η^1-C_5H_5 and hydride ligands from **15** is much more facile than reaction to give ketene complex **8**.

Experimental Section

General Data. Solvents were distilled from sodium 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 WP-200 (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 an 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.

(PMe)₃(NO)ReC(=C₅H₄)O (8) from Thermolysis of 4 and PMe₃. A tube containing a degassed toluene solution of **4** (320 mg, 0.986 mmol, 0.25 M) and PMe_3 (1.2 mL, 2.9 M) was sealed under vacuum at –196 °C and heated at 72 °C for 17 h. Methane was isolated in 44% yield from the reaction mixture by Toepler pump methods. Evaporation of the toluene and PMe_3 and recrystallization (THF–hexane) of the residue gave **8** as a yellow solid (150 mg, 28%): mp (sealed capillary) ≥175 °C dec; ^1H NMR (benzene-d_6) δ 1.05 (three-line pattern, $J_{PH+P'H}$ = 7.0 Hz, 18 H), 1.09 (d, J = 8.5 Hz, 9 H), 6.89 (m, J = 4.4, 1.8, 1.8 Hz, 1 H), 7.03 (m, J =4.4, 1.8, 1.6 Hz, 1 H), 7.20 (m, J = 4.4, 2.4, 1.6 Hz, 1 H), 7.30 (m, J = 4.4, 2.4, 1.8 Hz, 1 H); ^{13}C NMR (CD_2Cl_2, 0.09 M Cr-(acac)₃) δ 214.1 ($\nu_{1/2}$ = 29 Hz), 125.0 (d, J_{CH} = 162 Hz), 120.3, 119.0 (d, J_{CH} = 156 Hz), 118.0 (d, J_{CH} = 159 Hz), 112.3 (d, J_{CH} = 165 Hz), 21.10 (qd, J_{CH} = 127, J_{PC} = 28 Hz), 16.16 (qt, J_{CH} = 127, $J_{PC+P'C}$ = 37 Hz); ^{31}P NMR (benzene-d_6) δ –26.6 (d, J_{PP} = 8 Hz), –32.9 (t, J_{PP} = 8 Hz); IR (THF) 1621 (s), 1550 (s), 1420 (w), 1355 (m) cm⁻¹.

Anal. Calcd for $C_{15}H_{31}NO_2P_3Re$: C, 33.59; H, 5.83; N, 2.61. Found: C, 33.63; H, 5.83; N, 2.80.

MS, m/e calcd for $C_{15}H_{31}NO_2P_3^{187}Re$ 537.1121, obsd 537.1130. Molecular weight by osmometry in dichloroethane 502, calcd 536.

Methane: IR (neat) 3010 (s), 1307 (s) cm⁻¹; MS, m/e 16 (100), 15 (79.4), 14 (14.1), 13 (8.8).

8 from Photolysis of 4 and PMe₃. A tube containing a degassed toluene solution of **4** (858 mg, 2.64 mmol, 0.31 M) and PMe_3 (3.5 mL, 34.4 mmol, 4.0 M) was sealed under vacuum at –196 °C and photolyzed in a Rayonet photochemical reactor at λ_{max} = 366 nm for 112 h. Workup as above gave a 66% yield of methane and a 58% isolated yield of **8**.
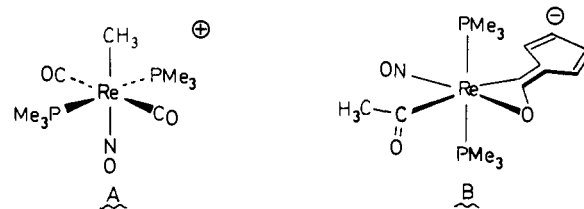
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(19) Grubbs has observed insertion of acetylene into the Ti–C bond of $[(\eta^5$-$C_5H_5)_2Ti(OCH=CH_2)]_n$ to give a similar ring-expanded product.[11]

In a related experiment, the ^{1}H NMR spectrum of a benzene-d_6 solution of **4** (0.12 M), PMe$_3$ (2.9 M), and 1,4-bis(trimethylsilyl)benzene (0.20 M) as internal standard indicated complete conversion of **4** to **5**, which was indefinitely stable at 32 °C in the dark. Photolysis of the sample at λ_{max} 366 nm and 32 °C for 80 h led to the formation of **8** in 67% NMR yield. In addition to resonances for **8**, equal intensity multiplets at δ 6.44, 6.27, and 2.71 were observed and are assigned to cyclopentadiene (30%).

(PMe$_3$)$_3$(NO)ReC(=C$_5$H$_4$)OC(CH$_3$)$_2$O (9). An acetone solution (20 mL) of **8** (286 mg, 0.53 mmol, 0.03 M) was stirred under nitrogen for 2 days at 26 °C. The solution was concentrated to 1 mL, hexane (4 mL) was added, and yellow solid **9** (291 mg, 0.49 mmol, 92%) was isolated by filtration. Recrystallization from acetone–hexane gave **9** as an analytically pure microcrystalline solid: mp (sealed capillary) 160–225 °C dec; ^{1}H NMR (benzene-d_6) δ 7.36 (m, 2 H), 6.96 (m, 1 H), 6.90 (m, 1 H), 1.36 (s, 6 H), 1.19 (three lines, $J_{PH+P'H}$ = 6.8 Hz, 18 H), 1.02 (d, J = 7.9 Hz, 9 H); ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 0.09 M Cr(acac)$_3$, –45 °C) δ 238.3 (d, J_{PC} = 55 Hz), 135.8, 122.5, 117.1, 116.4, 115.9, 109.3, 29.8, 18.0 (d, J_{PC} = 23 Hz), 15.0 (three-line pattern, $J_{P'C+PC}$ = 28 Hz); ^{31}P NMR (CD$_2$Cl$_2$, 0.09 M Cr(acac)$_3$, –40 °C) δ –34.1 (t, J_{PP} = 16 Hz), –38.9 (d, J_{PP} = 16 Hz); IR (THF) 1645 (vs), 1509 (m), 1355 (s) cm^{-1}.

Anal. Calcd for C$_{18}$H$_{37}$O$_3$NP$_3$Re: C, 36.36; H, 6.27; N, 2.36. Found: C, 36.26; H, 6.27; N, 2.35.

MS, m/e calcd for C$_{18}$H$_{37}$O$_3$NP$_3$^{187}Re 595.1538, obsd 595.1548.

Conversion of 9 to 8. An NMR tube containing a benzene-d_6 solution of **9** (24.2 mg, 0.04 mmol, 0.04 M) was placed in the probe of a Bruker WH-270 spectrometer maintained at 81 °C. Periodic observation by ^{1}H NMR indicated the clean conversion of **9** to **8** and free acetone with a half-life of 60 min.

(PMe$_3$)$_3$(NO)ReC(=C$_5$H$_4$)OC(CH$_3$)(CH$_2$CH$_3$)O (10). A 2-butanone solution (8 mL) of **8** (79 mg, 0.147 mmol, 0.018 M) was stirred for 2 days at 26 °C. The solution was concentrated to 1 mL, hexane (3 mL) was added, and **10** (58 mg, 0.095 mmol, 65%) was isolated as a brown solid: mp (sealed capillary) ≥170 °C dec; ^{1}H NMR (CD$_2$Cl$_2$) δ 6.61 (m, 1 H), 6.37 (m, 1 H), 6.06 (m, 1 H), 6.02 (m, 1 H), 1.61 (d, J = 8.1 Hz, 9 H), 1.50 (three-line pattern, $J_{PH+P'H}$ = 6.8 Hz, 9 H), 1.47 (three-line pattern, $J_{PH+P'H}$ = 6.8 Hz, 9 H), 1.21 (s, 3 H), 0.88 (t, J = 7 Hz, 3 H), the methylene protons were not observed. ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 0.09 M Cr(acac)$_3$, –40 °C) δ 238.4 (d, J_{PC} = 51 Hz), 136.0, 122.5, 118.2, 117.2, 116.3, 109.4, 35.2, 26.0, 18.1 (d, J = 23 Hz), 15.0 (three-line pattern, $J_{PC+P'C}$ = 28 Hz), 9.2. ^{31}P NMR (CD$_2$Cl$_2$, 0.09 M Cr(acac)$_3$, –40 °C) δ –33 (t, J_{PP} = 16 Hz), –39 (d, J_{PP} = 16 Hz); IR (THF) 1645 (vs), 1508 (s), 1355 (s) cm^{-1}. The mass spectrum of **10** showed a peak match for **8**. Apparently **10** dissociates to **8** and butanone in the mass spectrometer.

(PMe)$_3$(NO)(Cl)ReC(=C$_5$H$_4$)OH (11). On a vacuum line, HCl (0.27 mmol) was condensed into a THF (10 mL) slurry of **8** (143 mg, 0.27 mmol) at –78 °C and the solution was stirred at –78 °C for 30 min. The slurry was warmed to room temperature and concentrated to 1 mL. Hexane (3 mL) was added to give **11** as a yellow solid (131 mg, 0.23 mmol, 86%): mp (sealed capillary) 124–128 °C dec; ^{1}H NMR (CD$_2$Cl$_2$) δ 9.13 (d, J = 4.4 Hz, 1 H), 6.72 (m, 1 H), 6.51 (m, 1 H), 6.12 (m, 1 H), 6.07 (m, 1 H), 1.64 (d, J = 7.9 Hz, 9 H), 1.52 (three-line pattern, $J_{PH+P'H}$ = 7.8 Hz, 18 H); ^{13}C{^{1}H} NMR (THF-d_8, 0.09 M Cr(acac)$_3$) δ 219.3 (d, J_{PC} = 57 Hz), 140.8, 123.0, 121.6, 119.6, 113.1, 18.7 (d, J_{PC} = 24 Hz), 15.8 (three-line pattern, $J_{P'C+PC}$ = 34 Hz); ^{31}P NMR (THF-d_8) δ –34.8 (d, J_{PP} = 15 Hz), –41.6 (t, J_{PP} = 15 Hz); IR (THF) 3346 (br, w), 1671 (s), 1521 (s) cm^{-1}.

Anal. Calcd for C$_{15}$H$_{32}$ClNO$_2$P$_3$Re: C, 31.44; H, 5.63; N, 2.44. Found: C, 31.57; H, 5.85; N, 2.72.

Conversion of 11 to 8. A hexane solution of *n*-BuLi (0.12 mmol) was added by syringe to a –78 °C THF slurry (∼15 mL) of **11** (70 mg, 0.12 mmol). The slurry was warmed to room temperature, some solvent was evaporated, and hexane was added to give **8** as a yellow solid (51 mg, 0.095 mmol, 78%).

(PMe$_3$)$_3$Re(NO)(CO) (16). A tube containing a THF solution of (η^5-C$_5$H$_5$)Re(NO)(CO)(H) (14)[2b] (230 mg, 0.74 mmol, 0.09 M) and PMe$_3$ (0.45 g, 5.8 mmol, 0.68 M) was sealed under vacuum at –196 °C and heated at 80 °C for 15 min. Evaporation of volatile material and recrystallization (THF–hexane) of the residue gave **16** (280 mg, 0.6 mmol, 81%) as an analytically pure maroon solid. In a related experiment ^{1}H NMR of a benzene-d_6 solution of **14** (14.9 mg, 0.05 mmol, 0.13 M) and PMe$_3$ (2.7 M) indicated complete conversion of **14** to the η^1-C$_5$H$_5$ bis(phosphine) adduct **15** within 20 min at 22 °C. When this solution was heated at 50 °C for 20 min, the clean (≥95% by NMR) conversion of **15** to **16** and an equimolar amount of cyclopentadiene (equal intensity multiplets at δ 6.46, 6.27, and 2.69) was observed by ^{1}H NMR.

16: mp (sealed capillary) 105–110 °C dec; ^{1}H NMR (benzene-d_6) δ 1.35 (unresolved quartet); ^{13}C{^{1}H} NMR (benzene-d_6) δ 222.6, 23.5

(unresolved quartet); ^{31}P{^{1}H} (benzene-d_6) δ –42.2; IR (THF) 1820 (s), 1560 (s) cm^{-1}.

Anal. Calcd for C$_{10}$H$_{27}$NO$_2$P$_3$Re: C, 25.42; H, 5.76; N, 2.96. Found: C, 25.33; H, 5.56; N, 3.10.

15: ^{1}H NMR (benzene-d_6) δ 5.81 (t, J = 1.6 Hz, 5 H), 1.26 (d, J = 8.8 Hz, 9 H), 1.20 (d, J = 8.0 Hz, 9 H), 0.43 (dd, J = 56.7, 32.4 Hz, 1 H).

Formation of Bimetallic Compound 13. A 22-mL stainless steel bomb containing a benzene-d_6 solution of **5** (574 mg, 1.2 mmol, 0.6 M) and 600 psi of CO was heated at 90 °C for 4 h. ^{1}H NMR of the reaction mixture indicated the presence of (η^5-C$_5$H$_5$)Re(NO)(CH$_3$)(PMe$_3$), (η^5-C$_5$H$_5$)-Re(NO)(CH$_3$)(CO), (η^5-C$_5$H$_5$)Re(NO)(COCH$_3$)(PMe$_3$), and C$_5$H$_6$ in addition to resonances due to **13**. Volatile material was evaporated and the residue was chromatographed (30 × 2.5 cm silica gel, Et$_2$O). Evaporation of the second yellow band gave **13** as a yellow-orange analytically pure solid (105 mg, 0.11 mmol, 18% yield): mp (sealed capillary) 158–159 °C dec; ^{1}H NMR (acetone-d_6) δ 6.92 (m, 1 H), 6.38 (m, 1 H), 6.21 (m, 1 H), 6.06 (m, 1 H), 2.35 (s, 3 H), 1.86 (three-line pattern, $J_{PH+P'H}$ = 8.4 Hz, 18 H), 1.34 (three-line pattern, $J_{PH+P'H}$ = 7.6 Hz, 18 H), –0.69 (t, J = 10.7 Hz, 3 H); ^{13}C{^{1}H} NMR (THF-d_8, 12 °C) δ 238.1, 219.5, 205.7, 140.8, 127.6, 124.8, 122.6, 111.0, 50.8, 16.4 (three lines, $J_{PC+P'C}$ = 27 Hz), 14.6 (three lines, $J_{PC+P'C}$ = 26 Hz), –9.0; ^{31}P{^{1}H} NMR (15 °C, acetone-d_6) δ –26 (s), –36 (s); IR (Nujol) 1986 (s), 1692 (s), 1650 (s), 1545 (s), 1510 (m) cm^{-1}. Anal. Calcd for C$_{23}$H$_{46}$N$_2$O$_6$P$_4$Re$_2$: C, 29.30; H, 4.92; N, 2.97. Found: C, 28.92; H, 5.05; N, 3.00.

X-ray Structural Determination. A single crystal of **13**, obtained by slow evaporation of a saturated THF solution under an inert atmosphere, was mounted in a thin-walled glass capillary for the X-ray study. Preliminary examination of the crystal and collection of the diffraction data were carried out on a Syntex-Nicolet P$_1$ diffractometer equipped with a graphite monochromated Mo K$_\alpha$ radiation source (λ = 0.710 73 Å). Unit cell dimensions were determined from 15 accurately centered reflections ($24° < 2\theta < 28°$). The unit cell was found to be triclinic containing four molecules of the complex. Delaunay cell reduction did not reveal any cell of higher symmetry. Also, subsequent examination of the atomic coordinates did not reveal any missing symmetry. Structure amplitudes and their standard deviations were calculated from the intensity data by procedures similar to those described previously.[20] Absorption corrections were calculated by using an empirical spherical harmonic model.[21] Crystal data and details of the intensity data collection are given in Table II.

The structure was solved by direct methods using MULTAN and the 300 highest normalized structure factors. The E-map revealed the positions for the four rhenium atoms. A series of difference electron density maps

Table II. Summary of Crystal Data and Intensity Collection

empirical form	Re$_2$P$_4$O$_6$N$_2$C$_{23}$H$_{46}$
form wt	942.9
cryst dimens, mm	0.2 × 0.35 × 0.4
temp, K	293
cell params	
a, Å	18.328 (6)
b, Å	23.907 (7)
c, Å	8.751 (3)
α, deg	95.91 (2)
β, deg	101.98 (2)
γ, deg	111.33 (2)
space group	P_1
Z	4
density, calcd, g/cm^3	1.83
absorptn coeff, μ, cm^{-1}	69.6
scan range	
deg below 2θ K$_{\alpha1}$	0.9
deg above 2θ K$_{\alpha2}$	0.9
scan speed, deg/min	2.5–24.0
scan type	θ–2θ
2θ limits, deg	3.5–50.7
sin θ/λ_{max}, Å^{-1}	0.6
unique data	
measured	12522
$F_o > 3\sigma F_o$	8361
discrepency indices	
R_1	0.060
R_2	0.095
goodness of fit	2.75

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(21) Rae, A. D. *Acta Crystallogr.*, submitted for publication.

yielded positions for the rest of the nonhydrogen atoms. Several cycles of full-matrix isotropic least-squares refinement were carried out. Standard values for the atomic scattering factors including corrections for anomalous dispersion were employed throughout the structure analysis.[22] Thermal parameters for the methyl groups (1C(8) and 2C(8)) and the nitrosyl groups attached to 1Re(1) and 1Re(2) were excessive. A difference electron density map calculated with these methyl and nitrosyl atoms removed revealed positions consistent with disorder between the methyl and nitrosyl groups. The disordered positions were included in the model along with a constrained occupation factor for the disorder in each of the molecules. Constrained least-squares refinements were carried out using the program RAELS.[23] Idealized hydrogen atom positions were included for all hydrogens except those on the trimethylphosphine ligands. Each of the trimethylphosphine ligands was assumed to possess a reorientable thermal liberation axial system (TL model).[24]

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(22) Atomic form factors were from: Cromer, D. T.; Mann, J. B. "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. 4, pp 99–101, Table 2.2B. The atomic form factor for hydrogen was from: Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

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Least-squares refinement of this model using both strict[24] and slack[25] constraints converged with discrepancy indices $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ = 0.060 and $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2}$ = 0.095. The conventional R factor for the 47 data with $\sin \theta/\lambda < 0.1$ was 0.065. The final difference electron density map was featureless except for several peaks near the Re atoms. Additional X-ray tables for **13** are given in the supplementary material.

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Synthesis and Geometry Determination of Cofacial Diporphyrins. EPR Spectroscopy of Dicopper Diporphyrins in Frozen Solution

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Abstract: Frozen solution EPR spectra have been obtained for the dicopper complexes of six covalently linked diporphyrins whose synthesis is also described. The distance between the copper atoms in the diporphyrins was determined from the ratio of the intensity of the half-field transitions to the intensity of the allowed transitions and by computer simulation of the spectra. The values obtained by the two methods were in good agreement and ranged from 4.1 to 5.6 Å. The porphyrin planes were parallel within experimental uncertainty. The angle between the interspin vector and the normal to the porphyrin planes (slip angle) was determined by computer simulation of the spectra and values ranged from 20° to 45°. For the majority of the diporphyrins the separation between the porphyrin planes was 3.9 ± 0.1 Å. In an anthracene pillared diporphyrin the interplanar separation was 4.6 Å. These results were compared with those determined from crystal structures. Although there was no short bond pathway between the two copper atoms, the simulations of the spectra indicated that the absolute value of the copper–copper exchange interaction, J, was >0.3 cm^{-1}.

Binuclear metal complexes capable of coordinating and mediating electron transfer to dioxygen have become an important research area in contemporary bioinorganic chemistry. One class of such complexes is the dimeric porphyrins covalently linked in a cofacial configuration, the metal complexes of which are expected to be able to catalyze the 4-electron reduction of dioxygen to water in a manner possibly related to the terminal oxidase of the respiratory chain: cytochrome *c* oxidase.[2] The realization of this goal may also lead to the development of inexpensive electrode materials for electroreduction of dioxygen, which is of significant value to fuel cell technology.[3]

Cofacially linked dimeric porphyrins have been synthesized since 1977.[4] While variations now exist, one approach that has been used frequently is the double amide strapping of two diametrically substituted porphyrins.[5] This method, reported originally by one of the authors, provides a versatile approach to the synthesis of numerous diporphyrins with variable inter-ring distances. Such structural variability proved to be critical in directing the course of interactions between dioxygen and metallodiporphyrins. For example, binuclear cobalt and iron complexes of diporphyrins with five-, six-, and seven-atom linkages (DP-5, DP-6, DP-7) have been tested for their electroreduction response toward dioxygen when coated on a graphite electrode.[6] Invariably, peroxide was produced in these early investigations; the 4-electron process was not observed. In 1979 Collman and co-workers, using the same synthetic approach, obtained structurally equivalent face-to-face diporphyrins (FTF5 and FTF6).[7] Additionally they prepared

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(1) (a) Michigan State University. (2) University of Colorado at Denver. (c) University of Denver.

(2) Chang, C. K. In "Biochemical and Clinical Aspects of Oxygen"; Caughey, W. S, Ed.; Academic Press: New York, 1979; pp 437–454.

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(6) Chang, C. K. *Adv. Chem. Ser.* **1979**, *173*, 162–177.