

Data were corrected for absorption, although the correction may be poorly defined due to the very irregular shape of the fragment utilized. A final difference Fourier revealed several peaks of density 1.0 to 2.1 e/Å³ within 1.0 Å of the three metal atoms but was otherwise featureless.

W₄(CSiMe₃)₂(OEt)₁₄. A suitable small crystal was selected and transferred to the goniostat, where it was cooled to -155 °C. The crystal was characterized in the usual manner. A systematic search of a limited hemisphere of reciprocal space yielded a set of diffraction maxima which exhibited monoclinic symmetry and had systematic extinctions corresponding to the unique space group *P*₂₁/*n*.

The structure was solved by locating the two W atoms with direct methods, and the remainder of the non-hydrogen atoms were located in two successive difference Fouriers phased with the W atoms. The structure was refined by full-matrix least-squares with use of anisotropic thermal parameters on all atoms, and the hydrogen atoms were then located in a difference Fourier. Final refinements were completed with use of isotropic thermal parameters on the hydrogen atoms.

A final difference Fourier was essentially featureless, and a few peaks of ca. 0.8-1.0 e/Å³ were located in proximity to the W atoms.

The molecule contains a crystallographic center of inversion.

Acknowledgments. We thank the Department of Energy, Office of Basic Research, Chemical Sciences Division and the Wrubel Computing Center for support.

Note Added in Proof. We have recently found that W₄(μ-CSiMe₃)₂(OEt)₁₄ crystallizes from hexane in a second monoclinic form. Crystal data at -160 °C are as follows: *a* = 14.207 (8) Å, *b* = 10.821 (5) Å, *c* = 17.391 (11) Å, β = 97.69 (3)°, *Z* = 2, *d*_{calcd} = 1.926 g cm⁻³ in the space group *P*₂₁/*c*. All molecular dimensions are within 3σ. The two molecular structures are essentially superimposable.

Registry No. W₃(O-*i*-Pr)₉(CMe), 94499-61-3; W₄(μ-CSiMe₃)₂(OEt)₁₄, 94517-67-6; Mo₂W(CMe)(O-*i*-Pr)₉, 94499-62-4; W₂(O-*i*-Pr)₆(μ-C₄Me₄)(C₂Me₂), 87654-13-5; W₂(O-*i*-Pr)₆(Py)₂, 70178-75-5; (*t*-BuO)₃W≡CMe, 82209-23-2; Mo₂(O-*i*-Pr)₆, 62521-20-4; W₂(μ-CSiMe₃)₂(CH₂SiMe₃)₄, 59654-41-0; C₂Me₂, 503-17-3.

Supplementary Material Available: Complete listings of bond lengths and bond angles, anisotropic thermal parameters, and structure factor amplitudes (81 pages). Ordering information is given on any masthead page. The complete structural reports are available from the Indiana University Chemistry Library in microfiche form only at \$2.50 per report. Request MSC Report No. 84041 and 84047 for W₃(CMe)(O-*i*-Pr)₉ and W₄(CSiMe₃)₂(OEt)₁₄, respectively.

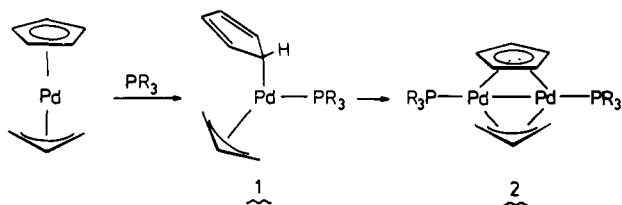
Interconversion of η⁵-C₅H₅, η¹-C₅H₅, and Ionic "η⁰"-C₅H₅ Rhenium Compounds—X-ray Crystal Structure of [Re(NO)(CH₃)(PMe₃)₄]⁺[C₅H₅]⁻

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Abstract: The reaction of (η⁵-C₅H₅)Re(NO)(CH₃)(PMe₃) (6) and PMe₃ produced (η¹-C₅H₅)Re(NO)(CH₃)(PMe₃)₃ (10). The reaction is reversible with *K*_{eq} = 0.4 M⁻² at 4 °C in THF-*d*₈. Upon heating at 48 °C in THF in the presence of high concentrations of PMe₃, the equilibrium mixture of 6 and 10 was converted to [Re(NO)(CH₃)(PMe₃)₄]⁺[C₅H₅]⁻ (9), which precipitates from solution. When 9 was heated in THF at 81 °C in the absence of added PMe₃, it was reconverted to 6 and free PMe₃. The structure of 9 was determined by X-ray crystallography: monoclinic space group *P*₂₁/*c*, with unit cell constants *a* = 12.893 (2) Å, *b* = 13.622 (2) Å, *c* = 15.068 (2) Å, β = 97.47 (2)°, and *Z* = 4.

The reactions of trialkylphosphines with η⁵-cyclopentadienyl transition-metal complexes result in a variety of interesting cyclopentadienyl ligand transformations. Werner reported that the reaction of (η⁵-C₅H₅)Pd(2-RC₃H₄) with P(*i*-Pr)₃ produced an η¹-C₅H₅ mono(phosphine) adduct 1 which reacted further to give the novel binuclear complex 2 in which the C₅H₅ ring spans two metals.¹

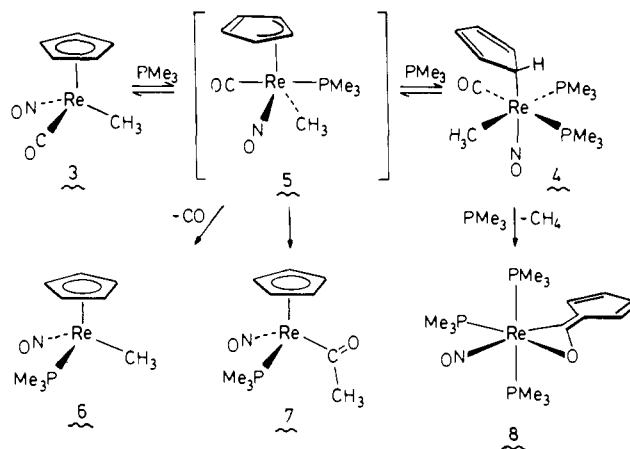


We have previously reported evidence for cyclopentadiene ring slippage (η⁵-C₅H₅ ⇌ η³-C₅H₅ ⇌ η¹-C₅H₅) during phosphine substitution reactions at coordinatively saturated metal centers.²

(1) Werner, H.; Tüne, D.; Parker, G.; Krüger, C.; Brauer, D. *J. Angew. Chem.* **1975**, *87*, 205-206. Werner, H.; Kuhn, A. *Angew. Chem.* **1979**, *91*, 447-448.

(2) (a) Casey, C. P.; Jones, W. D. *J. Am. Chem. Soc.* **1980**, *102*, 6154-6156. (b) Casey, C. P.; Jones, W. D.; Harsy, S. G. *J. Organomet. Chem.* **1981**, *206*, C38-C42. (c) Casey, C. P.; Andrews, M. A.; McAlister, D. R.; Jones, W. D.; Harsy, S. G. *J. Mol. Catal.* **1981**, *13*, 43-59. (d) Casey, C. P.; O'Connor, J. M.; Jones, W. D.; Haller, K. J. *Organometallics* **1983**, *2*, 535-538. (e) Casey, C. P.; O'Connor, J. M. *Organometallics*, submitted.

Scheme 1



Thus, (η⁵-C₅H₅)Re(NO)(CH₃)(CO) (3) reacted rapidly and reversibly with 2 equiv of PMe₃ at 25 °C to give the η¹-C₅H₅ bis(phosphine) adduct 4 via a proposed η³-C₅H₅ mono(phosphine) intermediate 5. When benzene-*d*₆ solutions of 4 were heated to 90 °C an equilibrium mixture of 3 and 4 was slowly converted to a 4:1 (50%) mixture of phosphine-substituted methyl and acetyl complexes, 6 and 7, probably via the same η³-C₅H₅ intermediate

Table I. Interatomic Distances (Å) and Angles (deg) for **9**^a

		Distances			
Re-P(1)	2.454 (1)	P(2)-C(5)	1.826 (5)	C(15)-C(16)	1.395 (8)
Re-P(2)	2.442 (1)	P(2)-C(6)	1.817 (5)	C(16)-C(17)	1.398 (8)
Re-P(3)	2.436 (1)	P(2)-C(7)	1.822 (5)	C(17)-C(18)	1.399 (8)
Re-P(4)	2.425 (1)	P(3)-C(8)	1.828 (5)	C(18)-C(14)	1.403 (7)
Re-C(1)	2.172 (14)	P(3)-C(9)	1.825 (5)	C(14)-H(14)	1.10 (6)
Re-N	1.800 (8)	P(3)-C(10)	1.810 (6)	C(15)-H(15)	1.09 (6)
N-O	1.220 (9)	P(4)-C(11)	1.822 (6)	C(16)-H(16)	0.94 (7)
P(1)-C(2)	1.822 (5)	P(4)-C(12)	1.827 (6)	C(17)-H(17)	1.18 (7)
P(1)-C(3)	1.813 (5)	P(4)-C(13)	1.828 (5)	C(18)-H(18)	1.04 (6)
P(1)-C(4)	1.810 (5)	C(14)-C(15)	1.402 (7)		
		Angles			
P(1),Re,P(2)	91.57 (4)	P(3),Re,C(1)	95.90 (34)	Re,P(1),C(2)	117.61 (18)
P(1),Re,P(3)	169.37 (4)	P(3),Re,N	82.45 (26)	Re,P(1),C(3)	114.02 (19)
P(1),Re,P(4)	90.20 (4)	P(4),Re,C(1)	85.00 (34)	Re,P(1),C(4)	118.17 (20)
P(1),Re,C(1)	94.72 (34)	P(4),Re,N	96.06 (24)	Re,P(2),C(5)	115.22 (19)
P(1),Re,N	86.93 (26)	C(1),Re,N	178.05 (43)	Re,P(2),C(6)	118.98 (17)
P(2),Re,P(3)	90.03 (4)	Re,N,O	176.87 (68)	Re,P(2),C(7)	118.25 (18)
P(2),Re,P(4)	164.08 (4)	C(18),C(14),C(15)	107.78 (48)	Re,P(3),C(8)	115.16 (18)
P(2),Re,C(1)	79.09 (34)	C(14),C(15),C(16)	107.96 (46)	Re,P(3),C(9)	115.85 (16)
P(2),Re,N	99.82 (24)	C(15),C(16),C(17)	108.33 (51)	Re,P(3),C(10)	118.85 (20)
P(3),Re,P(4)	91.14 (4)	C(16),C(17),C(18)	107.87 (49)	Re,P(4),C(11)	115.47 (18)
		C(14),C(18),C(17)	108.05 (49)	Re,P(4),C(12)	118.61 (22)
				Re,P(4),C(13)	116.35 (20)

^a The estimated standard deviation of the least significant digit is given in parentheses.

5. When conversion to **6** and **7** was inhibited by high concentrations of PMe_3 , another reaction leading to cyclopentadienylidene ketene complex **8** took place.³

Here we report that when **3** is heated with high concentrations of PMe_3 in THF, the cyclopentadienyl ligand is completely cleaved from rhenium and the tetrakis(phosphine) adduct $[\text{Re}(\text{NO})(\text{CH}_3)(\text{PMe}_3)_4]^+[\text{C}_5\text{H}_5]^-$ (**9**) is isolated in 9% yield.⁴ The ionic " η^0 "- C_5H_5 compound **9** is also formed in 45% yield when $(\eta^1\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{CH}_3)(\text{PMe}_3)_3$ (**10**) is heated with high concentrations of PMe_3 . When the " η^0 "- C_5H_5 compound **9** is heated in THF in the absence of PMe_3 , reformation of the rhenium-cyclopentadienyl linkage takes place and $\eta^5\text{-C}_5\text{H}_5$ complex **6** is obtained.

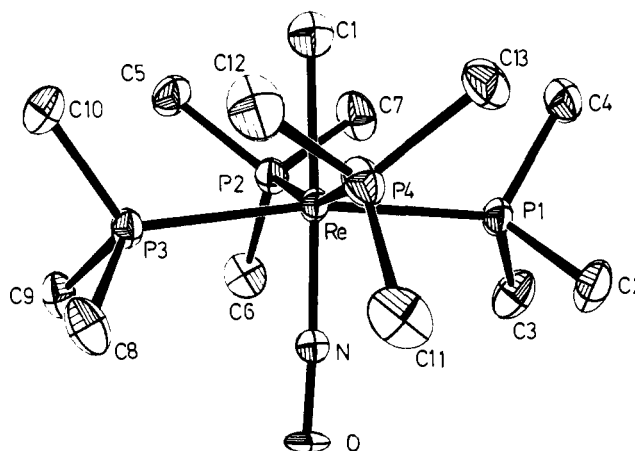
Results

Synthesis of $[\text{Re}(\text{NO})(\text{CH}_3)(\text{PMe}_3)_4]^+[\text{C}_5\text{H}_5]^-$ (9**) from $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{CH}_3)(\text{CO})$ (**3**).** Reaction of **3** with 4 M PMe_3 for 29 h in THF at 70 °C led to precipitation of yellow crystalline $[\text{Re}(\text{NO})(\text{CH}_3)(\text{PMe}_3)_4]^+[\text{C}_5\text{H}_5]^-$ (**9**) in 9% isolated yield. ¹H NMR of the residue from evaporation of PMe_3 and THF indicated the presence of ketene complex **8**, compounds **11** and **12** (see below), and a small amount of **6** in addition to numerous unassigned resonances.

Crystalline **9** is insoluble in hexane, Et_2O , and THF and decomposes rapidly in acetone and CH_2Cl_2 . Acetonitrile solutions of **9** are stable for days at -30 °C or for hours at 25 °C.

The structure of **9** was assigned on the basis of spectral evidence and was later confirmed by X-ray crystallography. The ¹H NMR of **9** in CD_3CN consists of a singlet at δ 5.48 (5 H), assigned to the C_5H_5^- counterion, a three-line pattern at 1.64 ($J_{\text{PH}+\text{PH}} = 6.6$ Hz, 36 H), assigned to the four equivalent PMe_3 ligands, and a quintet at -1.00 ($J_{\text{PH}} = 10.7$ Hz, 3 H), assigned to the CH_3Re unit coupled to the four equivalent phosphines. In the ¹³C NMR of **9**, the C_5H_5^- anion gives rise to a singlet at δ 104.1.

The C_5H_5^- ion of **9** undergoes slow deuterium exchange with the CD_3CN solvent at 25 °C. Thus, within hours at 25 °C in CD_3CN , the δ 5.48 singlet of **9** disappears while the resonances due to the $[\text{Re}(\text{NO})(\text{CH}_3)(\text{PMe}_3)_4]^+$ cation remain unchanged. ²H NMR (CH_3CN , -30 °C) of the deuterated compound, **9**- d_5 , shows a singlet at δ 5.5. Compound **9**- d_5 is cleanly converted back to **9** in CH_3CN at 25 °C.

**Figure 1.** ORTEP diagram of the $[\text{Re}(\text{NO})(\text{CH}_3)(\text{PMe}_3)_4]^+$ portion of **9**.**Table II.** Least-Squares Planes for **9**

atoms	dev	atoms	dev
Plane I		Plane II	
C(14)	0.0014	Re	-0.0442
C(15)	0.0016	P(1)	-0.2688
C(16)	-0.0039	P(2)	0.2913
C(17)	0.0047	P(3)	-0.2725
C(18)	0.0038	P(4)	0.2942

The IR spectrum of **9** (KBr) shows strong overlapping bands at 1648 and 1670 cm^{-1} assigned to the terminal nitrosyl ligand in **9**. Bands due to the C_5H_5^- ion are observed at 3040 (m, $\nu_{\text{C-H}}$), 1000 (m, $\delta_{\text{C-H}}$), and 673 (shoulder, $\gamma_{\text{C-H}}$) cm^{-1} . These latter three bands are not observed in the IR (KBr) of **9**- d_5 which has new bands at 2258 (m, $\nu_{\text{C-D}}$) and 761 (m, $\delta_{\text{C-D}}$) cm^{-1} .

X-ray Structure of $[\text{Re}(\text{NO})(\text{CH}_3)(\text{PMe}_3)_4]^+[\text{C}_5\text{H}_5]^-$. The C_5H_5^- counterion formulation for **9** was demonstrated by X-ray crystallographic analysis (Figures 1 and 2; Tables I and II). The cation portion of **9** has approximately octahedral geometry with the CH_3 and NO ligands in trans positions and a $\text{CH}_3\text{-Re-N}$ angle of 177°. The nitrosyl ligand is nearly linear with a Re-N-O angle of 177°. One pair of trans phosphine ligands is bent downward with a P(1)-Re-P(3) angle of 169°, while the other pair of trans phosphine ligands is bent upward with a P(2)-Re-P(4) angle of 164°. Similar distortions from octahedral symmetry have been observed in other tetrakis(trimethylphosphine) complexes⁵ and

(3) Casey, C. P.; O'Connor, J. M. *J. Am. Chem. Soc.* **1983**, *105*, 2919-2920.

(4) A related reaction has recently been reported for $(\text{C}_3\text{Ph}_4\text{H})\text{GeMe}_2\text{Cl}$: Borisova, I. V.; Luzikov, Y. N.; Zemlyansky, N. N.; Utsyniyuk, Y. A.; Beltskaya, I. P. *J. Organomet. Chem.* **1984**, *268*, 11-17.

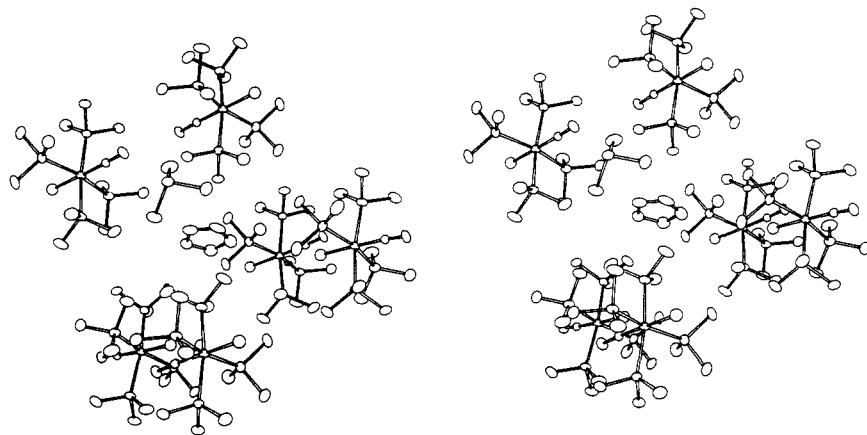
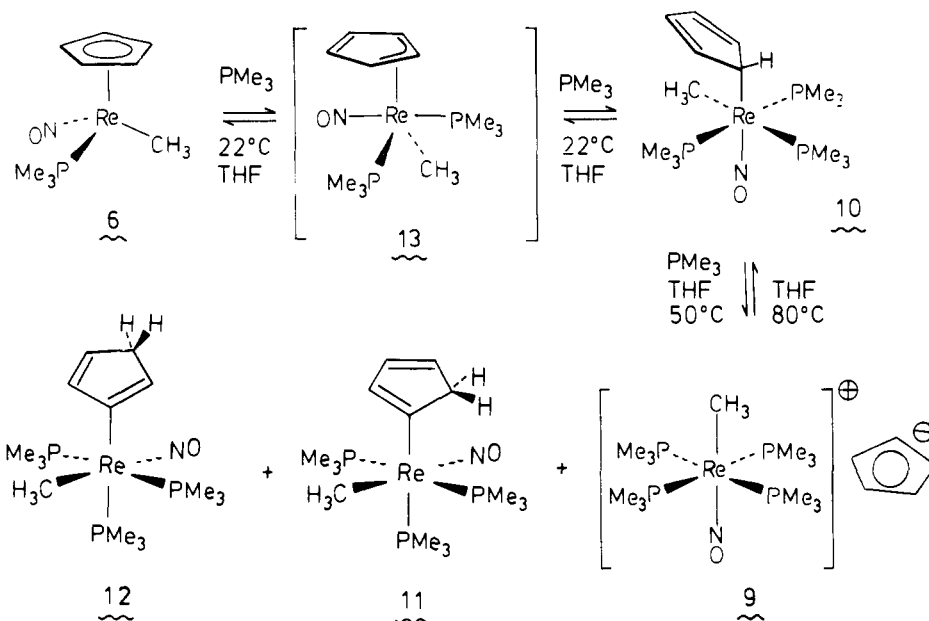


Figure 2. Stereoview showing a sphere of enclosure about the $C_5H_5^-$ unit of **9**.

Scheme II



are attributed to relief of steric crowding due to four bulky in-plane phosphine ligands. The anion portion of **9** is essentially planar; the largest deviation of carbon from the mean plane is 0.005 Å (Table II). The average C–C bond distance in the $C_5H_5^-$ unit is 1.399 (8) Å, and the average C–C–C angle is 108.0 (5)°. For comparison, benzene is reported to have an average C–C bond length of 1.399 (1) Å⁶ and $Na(TMEDA)^+C_5H_5^-$ is reported to have an average C–C bond length of 1.38 (2) Å.^{7a}

The $C_5H_5^-$ anion occupies crystal lattice sites surrounded by an octahedral array of PMe_3 ligands on rhenium cations; the closest distance between cation and anion is the C(2)–C(15) distance of 3.65 Å between a carbon of the $C_5H_5^-$ anion and a carbon of a PMe_3 ligand (Figure 2). Thus, the $C_5H_5^-$ anion of **9** is in an essentially hydrocarbon environment.

Other metal cyclopentadienide compounds which have been characterized crystallographically show $\eta^5-C_5H_5^-$ bonding to the metal counterion. For example, $Na(TMEDA)^+C_5H_5^-$ consists of puckered chains of Na atoms linked together by bridging $\eta^5-C_5H_5^-$ groups.^{7a} The carbon atoms are an average distance of

2.92 (1) Å from the sodium atoms. Similar structures are also found for $Pb(C_5H_5)_2$,^{7b} $Tl(C_5H_5)$,^{7c} and $In(C_5H_5)$.^{7c}

Formation of $(\eta^1-C_5H_5)Re(NO)(CH_3)(PMe_3)_3$ (10**) from $(\eta^5-C_5H_5)Re(NO)(CH_3)(PMe_3)_3$ (**6**) and PMe_3 .** Reaction of **6** and 8 M PMe_3 in hexane at 22 °C for 6 h led to isolation of $(\eta^1-C_5H_5)Re(NO)(CH_3)(PMe_3)_3$ (**10**) as a yellow solid in quantitative yield. Solid **10** decomposes over the course of days at 22 °C under either nitrogen or vacuum. In THF solution at 22 °C, **10** is rapidly converted to **6** and free PMe_3 . Spectroscopic characterization was therefore performed on 1:1 $PMe_3:THF-d_8$ solutions of **10** where the high PMe_3 concentration favors **10** over **6**. The ¹H NMR of **10** establishes the presence of two equivalent trans PMe_3 ligands (δ 1.51, three lines, $J_{PH+PH} = 7.0$ Hz) and one unique PMe_3 ligand (δ 1.47, d, $J_{PH} = 7.2$ Hz). The methyl group in **10** appears at δ 0.59 as a triplet of doublets with a large cis coupling (8.2 Hz) to the two equivalent phosphines and a small trans coupling (2.0 Hz) to the unique phosphine. These coupling constants require that the methyl and PMe_3 ligands all occupy the same plane. Consistent with this formulation is the observation of a quartet at δ 5.44 ($J = 1.4$ Hz) for the fluxional $\eta^1-C_5H_5^-$ ligand. For comparison, 1.3 to 1.5 Hz coupling constants have been observed for phosphorus ligands cis to $\eta^1-C_5H_5^-$ ligands in a number of related complexes.² In the ¹³C NMR of **10** the fluxional $\eta^1-C_5H_5^-$ ligand gives rise to a singlet at δ 114.1. The IR spectrum (KBr) of **10** has a band at 1628 cm^{-1} assigned to a linear nitrosyl ligand.

The reversibility of the formation of **10** was demonstrated by preparing a $THF-d_8$ solution of **10** at –78 °C and by obtaining its ¹H NMR spectrum at –53 °C which indicated a 32:1 ratio

(5) Carmona, E.; Marin, J. M.; Poveda, M. L.; Atwood, J. L.; Rogers, R. D. *J. Am. Chem. Soc.* **1983**, *105*, 3014–3022.

(6) Tamagawa, K.; Iijima, T.; Kimura, M. *J. Mol. Struct.* **1976**, *30*, 243–253 and references therein.

(7) (a) Aoyagi, T.; Shearer, H. M. M.; Wade, W. J. *Chem. Soc., Chem. Commun.* **1976**, 164–165. Aoyagi, T.; Shearer, H. M. M.; Wade, K.; Whitehead, G. J. *Organomet. Chem.* **1979**, *175*, 21–31. (b) Panattoni, C.; Bombieri, G.; Croatto, U. *Acta Crystallogr.* **1966**, *21*, 823–826. (c) Frasson, E.; Menegus, F.; Panattoni, C. *Nature (London)* **1963**, *199*, 1087–1089.

of **10** to **6**. When the sample was warmed to 25 °C for 1 h, ¹H NMR indicated complete conversion of **10** to **6** and free PMe₃.

To measure the equilibrium constant for the interconversion of **6** and **10**, a solution of **6** (0.16 M) and PMe₃ (1.2 M) in THF-*d*₈ was maintained at 4.0 ± 0.1 °C and the concentrations of **6**, **10**, and PMe₃ were monitored by ¹H NMR spectroscopy at -78 °C. Equilibration was established within 7 days and the equilibrium constant, $K = [\mathbf{10}][\mathbf{6}]^{-1}[\text{PMe}_3]^{-2}$, was found to be 0.4 M⁻² at 4 °C. For comparison, ($\eta^5\text{-C}_5\text{H}_5$)Re(NO)(CH₃)(CO), (**3**), reacts reversibly with PMe₃ to form the substantially more thermodynamically stable $\eta^1\text{-C}_5\text{H}_5$ bis(phosphine) adduct **4** ($K = 710 \text{ M}^{-2}$ in THF at 25.0 °C).^{2a}

Synthesis of 9 from ($\eta^5\text{-C}_5\text{H}_5$)Re(NO)(CH₃)(PMe₃) (6**) and PMe₃.** In the hope of obtaining a higher yield route to " $\eta^0\text{-C}_5\text{H}_5$ " compound **9**, we examined the reaction of ($\eta^5\text{-C}_5\text{H}_5$)Re(NO)(CH₃)(PMe₃) (**6**) with high concentrations of PMe₃. When a THF solution of **6** and 5 M PMe₃ was heated at 50 °C for 17 days, yellow crystalline needles of **9** formed in 45% yield.

When this solution was evaporated, a yellow solid was obtained in 45% yield which was tentatively formulated as a 1:1 mixture of **11** and **12**.⁸ These products are formally the result of 1,5-hydrogen shifts around the rhenium-substituted cyclopentadiene ring. The composition of **11** and **12** was clearly established by converting the isolated mixture of **11** and **12** to a 2:1 mixture of PMe₃:**6** by heating a 0.08 M benzene-*d*₆ solution of **11** and **12** at 80 °C for 24 h. In the ¹H NMR of the mixture of **11** and **12** at 47 °C, six multiplets of nearly equal intensity are seen between δ 5.8 and 6.8 which are assigned to the three vinyl hydrogens in each of the complexes. The methylene groups on the C₅ ligands of **11** and **12** are accidentally degenerate and appear as a broad singlet at δ 2.9. Each of the complexes has a meridional arrangement of three PMe₃ ligands which give rise to a doublet for the unique PMe₃ (δ 1.52, 1.51) and a pseudotriplet for the trans PMe₃ ligands (δ 1.32, 1.29). The methyl groups of **11** and **12** are accidentally degenerate and appear as a doublet of triplets ($J = 13, 10 \text{ Hz}$) at δ -0.97; the large and nearly equal magnitude of these coupling constants requires that the methyl group be cis to all three PMe₃ ligands in each of the complexes. The large ³¹P-¹³C coupling of the rhenium-bound carbon of the C₅ rings of **11** and **12** (δ 173.3, $J = 50 \text{ Hz}$; δ 165.6, $J = 45 \text{ Hz}$) observed in the ¹³C NMR spectrum establishes a trans relationship between the C₅ rings and a PMe₃ ligand. The linear nitrosyl ligands of **11** and **12** give rise to a single IR band at 1608 cm⁻¹. At low temperature, the ¹H NMR is substantially more complex presumably due to slow rotation about the rhenium to C₅ ring bond and to the presence of rotational isomers (see Experimental Section).

Reformation of the Cyclopentadiene-Rhenium Bond. When the " $\eta^0\text{-C}_5\text{H}_5$ " salt **9** was heated in THF-*d*₈ at 80 °C for 4 days, the yellow solid slowly dissolved and was cleanly converted to $\eta^5\text{-C}_5\text{H}_5$ compound **6** and 3 equiv of free PMe₃ as determined by ¹H NMR and IR spectroscopy.

Discussion

Previously we have reported that ($\eta^5\text{-C}_5\text{H}_5$)Re(NO)(CH₃)(CO) (**3**) reacts rapidly and reversibly with PMe₃ at 25 °C to give ($\eta^1\text{-C}_5\text{H}_5$)Re(NO)(CH₃)(CO)(PMe₃)₂, (**4**) via a C₅H₅ mono(phosphine) intermediate, **5**.^{2a} Although we cannot rule out a bent-nitrosyl mono(phosphine) structure for **5**, we favor an $\eta^3\text{-C}_5\text{H}_5$ formulation since it provides a smooth transition from η^5 -complex **3** to η^1 -complex **4** and because we have previously demonstrated in the case of ($\eta^5\text{-C}_5\text{H}_5$)Re(CO)₃ that nitrosyl ligands are not required for the formation of $\eta^1\text{-C}_5\text{H}_5$ bis(phosphine)rhenium complexes.^{2d} In 1969, Cotton⁹ reported the X-ray crystal structure of (C₅H₅)₃MoNO for which an ($\eta^1\text{-C}_5\text{H}_5$)($\eta^3\text{-C}_5\text{H}_5$)($\eta^5\text{-C}_5\text{H}_5$)-

MoNO formulation seemed plausible on the basis of the 18-electron rule. However, the structure was shown to consist of an ($\eta^1\text{-C}_5\text{H}_5$)(NO)Mo unit and two additional cyclopentadienyl ligands in which all ten carbons had significant bonding interactions with molybdenum. Cotton noted that simple geometry requires that a metal atom equidistant from three carbons of a regular planar pentagonal cyclopentadienyl ligand is necessarily equidistant from all five ring carbons. This makes $\eta^3\text{-C}_5\text{H}_5$ and $\eta^5\text{-C}_5\text{H}_5$ geometries indistinguishable, and Cotton stated that "the concept of a (trihapto-cyclopentadienyl)metal bond...is mythical". However, this rationale leaves open the possibility of a nonplanar $\eta^3\text{-C}_5\text{H}_5$ ligand. In 1978, Huttner, Brintzinger, and Bell¹⁰ reported the crystal structure of ($\eta^5\text{-C}_5\text{H}_5$)($\eta^3\text{-C}_5\text{H}_5$)W(CO)₂ in which there was a 20° angle between the planes of the allyl group and the alkene group in the $\eta^3\text{-C}_5\text{H}_5$. In light of the above discussion, we believe that intermediate **5** contains a bent $\eta^3\text{-C}_5\text{H}_5$ ligand.

When the equilibrating mixture of **3** and **4** was heated at 90 °C in benzene, it was slowly converted to a 4:1 mixture of phosphine-substituted methyl and acetyl complexes, **6** and **7**, probably via the same $\eta^3\text{-C}_5\text{H}_5$ intermediate **5**. When conversion to **6** and **7** was inhibited by high concentrations of PMe₃, a different reaction leading to cyclopentadienyldene ketene complex **8** took place.³ Complex **8** is formally the result of a CO insertion into the $\eta^1\text{-C}_5\text{H}_5$ -rhenium bond followed by loss of a cyclopentadienyl hydrogen. In the work reported here, we have found still another product from the reaction of **3** with PMe₃. When **3** and high concentrations of PMe₃ were heated in THF, the cyclopentadienyl ligand was completely severed from rhenium and the ionic " $\eta^0\text{-C}_5\text{H}_5$ " compound **9** crystallized in low yield from hot THF.

The ionic " $\eta^0\text{-C}_5\text{H}_5$ " compound **9** is formed more cleanly and in higher yield from reaction of ($\eta^5\text{-C}_5\text{H}_5$)Re(NO)(CH₃)(PMe₃) (**6**) and high concentrations of PMe₃ at 50 °C. Under milder conditions, the $\eta^1\text{-C}_5\text{H}_5$ intermediate **10** was isolated. When a THF solution of **6** and 4 M PMe₃ was monitored by ¹H NMR, the clean conversion to $\eta^1\text{-C}_5\text{H}_5$ tris(phosphine) complex **10** was observed. Complex **10** was isolated but is stable in solution only in the presence of high concentrations of PMe₃; in dilute solution, **10** dissociates PMe₃ and reforms **6**. By analogy to the reaction of **3** with PMe₃ to give **4**, we believe that the conversion of **6** to **10** involves an $\eta^3\text{-C}_5\text{H}_5$ intermediate, **13**. Remarkably, when solid ionic " $\eta^0\text{-C}_5\text{H}_5$ " compound **9** was heated in THF, it slowly dissolved to reform $\eta^5\text{-C}_5\text{H}_5$ complex **6**. Presumably this reaction proceeds via dissociation of PMe₃ from **9** and formation of a Re-cyclopentadienyl bond to generate observed $\eta^1\text{-C}_5\text{H}_5$ intermediate **10** which then dissociates a second phosphine to generate the postulated intermediate $\eta^3\text{-C}_5\text{H}_5$ complex **13** and finally dissociates a third PMe₃ ligand to give the isolated $\eta^5\text{-C}_5\text{H}_5$ complex **6**. We believe that this reversible interconversion of η^5 , η^3 , η^1 , and ionic " $\eta^0\text{-C}_5\text{H}_5$ " compounds is unprecedented.

Displacement of a coordinated C₅H₅ ligand by a neutral incoming ligand has been observed before;¹¹ however, products containing a C₅H₅ counterion have not been well characterized. In 1966, Behrens and Meyer speculated that (C₅H₅)₂Ni might reversibly dissociate to [Ni(NH₃)₆]²⁺[C₅H₅]₂⁻ in liquid ammonia.¹² In 1979, Booth and Smith reported that the reaction of (C₅H₅)₂Ni and 2 equiv of CH₂=PPh₃ gave an air-sensitive brown precipitate which, although itself uncharacterized, gave [($\eta^5\text{-C}_5\text{H}_5$)Ni(CH₂PPh₃)₂]⁺[BPh₄]⁻ upon treatment with NaBPh₄.¹³ Most recently Fabian and Labinger reported that ($\eta^5\text{-C}_5\text{H}_5$)($\eta^1\text{-C}_5\text{H}_5$)Fe(CO)₂ reacts rapidly with PMe₃ to give a yellow precipitate, which they formulated as [($\eta^5\text{-C}_5\text{H}_5$)Fe(CO)(PMe₃)₂]⁺[C₅H₅]⁻ on the basis of its reactions with water and CHCl₃.¹⁴ Due to the poor solubility of the compound in polar

(8) Related platinum complexes and 1-silyl-, 2-silyl-, and 3-silylcyclopentadiene isomers have been reported in the literature. For leading references see: Egger, K. W.; James, T. L. *J. Organomet. Chem.* **1971**, *26*, 335-343. Cuthberston, A. F.; Glidewell, C. *J. Organomet. Chem.* **1981**, *221*, 19-31. Boag, N. M.; Goodfellow, R. J.; Green, M.; Hessner, B.; Howard, J. A. K.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1983**, 2585-2591.

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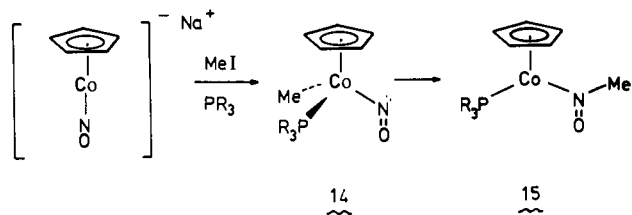
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solvents, the only spectroscopic characterization was an IR (Nujol) band at 1940 cm^{-1} .

It is interesting to note that we found no evidence for the insertion of the nitrosyl ligand into either the rhenium-methyl or the rhenium- $\eta^5\text{-C}_5\text{H}_5$ bonds of **10** or **13**. Bergman has recently reported that $\text{Na}^+[(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{NO})]^-$ reacts with MeI in the presence of PET_3 at -60°C to give $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{NO})(\text{Me})(\text{PET}_3)$ (**14**), which upon warming to room temperature gave nitrosoalkane complex **15**.¹⁵ In this reaction a bending of the nitrosyl ligand and not an $\eta^5\text{-C}_5\text{H}_5$ to $\eta^3\text{-C}_5\text{H}_5$ ring transformation maintains the 18-electron count at the metal in **14**.



Since the classic work on ferrocene first appeared over a quarter of a century ago,¹⁶ the η^5 -cyclopentadienyl ligand has become one of the most extensively utilized ligands in organotransition metal chemistry. We therefore find the PMe_3 -induced $\eta^5 \rightleftharpoons \eta^3 \rightleftharpoons \eta^1 \rightleftharpoons \eta^0$ cyclopentadienyl transformations reported here a fascinating addition to the known chemical reactivity of this important ligand.

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.

$(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{CH}_3)(\text{PMe}_3)$ (**6**). A solution of $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{CO})(\text{NO})(\text{CH}_3)$ (**3**) (98 mg, 0.30 mmol) and PMe_3 (0.91 mmol, 1.8 M) in 0.5 mL of benzene was heated at 90°C for 1 h in a sealed tube. Solvent and excess PMe_3 were pumped off, and the residue was thin-layer chromatographed (silica gel- Et_2O) under nitrogen to give **6** as an orange solid (44 mg, 0.12 mmol, 39%): mp (sealed capillary) $90\text{--}91^\circ\text{C}$ dec; ^1H NMR ($\text{THF-}d_8$) δ 5.07 (s, 5 H), 1.57 (d, $J = 9.7$ Hz, 9 H), 0.70 (d, $J = 6.4$ Hz, 3 H); $^{13}\text{C}\{^1\text{H}\}$ NMR ($\text{THF-}d_8$, -50°C) δ 87.5, 18.4 (d, $J = 35$ Hz), -41.4 (d, $J = 5$ Hz); ^{31}P NMR ($\text{THF-}d_8$, -50°C) δ -29.8 ; IR (THF) 1650 cm^{-1} .

Anal. Calcd for $\text{C}_9\text{H}_{17}\text{NOPRe}$: C, 29.03; H, 4.60; N, 3.76. Found: C, 29.34; H, 4.83; N, 3.93.

$(\eta^1\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{CH}_3)(\text{PMe}_3)_3$ (**10**). A hexane:trimethylphosphine (0.5:2.0 mL) solution of **6** (97 mg, 0.26 mmol, 0.13 M) was stirred at 22°C for 6 h. Evaporation of solvent led to isolation of **10** as a yellow solid in quantitative yield (143 mg, 104%). Solid **10** decomposes at 22°C in a sealed evacuated vial over the course of days. ^1H NMR (1:1, $\text{THF-}d_8\text{-PMe}_3$) δ 5.44 (q, $J = 1.4$ Hz, 5 H), 1.51 (3 lines, $J_{\text{PH}+\text{PH}} = 7.0$ Hz, 18 H), 1.47 (d, $J_{\text{PH}} = 7.2$ Hz, 9 H), 0.59 (td, $J = 8.2, 2.0$ Hz, 3 H); $^{13}\text{C}\{^1\text{H}\}$ NMR (1:1, $\text{THF-}d_8\text{-PMe}_3$, -50°C) δ 114.1, 21.1 (d, $J_{\text{PC}} = 28$ Hz), 16.4 (t, $J_{\text{PC}} = 14$ Hz), -8.9 (br); ^{31}P NMR (1:1, $\text{THF-}d_8\text{-PMe}_3$, -50°C) δ -42.1 (d, $J_{\text{PP}} = 8$ Hz), -57.7 (t, $J_{\text{PP}} = 8$ Hz); IR (KBr) 1678 cm^{-1} .

Interconversion of 6 and 10. On a high-vacuum line, PMe_3 (0.2 mL) was condensed into an NMR tube containing **6** (16 mg, 0.04 mmol) and the solution was maintained at 22°C for 3 h. PMe_3 was then evaporated to give **10** as a yellow oil. $\text{THF-}d_8$ was distilled into the tube at -78°C , and the tube was sealed under vacuum and placed in the precooled (-53

$^\circ\text{C}$) probe of a Bruker 270-MHz NMR spectrometer. ^1H NMR indicated a 32:1 ratio of **10** to **6** in addition to some free PMe_3 . The sample was warmed to 25°C for 1 h at which time ^1H NMR indicated complete conversion of **10** to **6** and PMe_3 .

Equilibration of 6 and 10. A sealed NMR tube containing **6** (17.2 mg, 0.046 mmol), PMe_3 (0.34 mmol), and $\text{THF-}d_8$ (total volume 0.28 mL at 25°C) was placed in a $4.0 \pm 0.1^\circ\text{C}$ constant-temperature bath. The concentrations of **6** and **10** were periodically monitored by -78°C ^1H NMR. Complete equilibration occurred within 7 days to produce a solution containing 0.051 M **3**, 0.11 M **10**, and 1.05 M PMe_3 ; $K_{\text{eq}} = [\text{10}][\text{6}]^{-1}[\text{PMe}_3]^{-2} = 0.4\text{ M}^{-2}$.

$[\text{Re}(\text{NO})(\text{CH}_3)(\text{PMe}_3)_4]^+[\text{C}_5\text{H}_5]^-$ (**9**) from **6** and PMe_3 . A sealed tube containing a solution of **6** (278 mg, 0.74 mmol) and PMe_3 (7.5 mL, 74 mmol, 4.9 M) in THF (7.5 mL) was heated at 50°C for 17 days. Yellow crystalline **9** (203 mg, 45%) formed during the course of reaction and was isolated by filtration as analytically pure material. Evaporation of the mother liquor gave a yellow solid which was shown by ^1H NMR to be a mixture of **11** and **12** (171 mg, 45%). **11** and **12** could not be separated by recrystallization or by reverse phase HPLC and decomposed upon attempted silica gel or alumina thin-layer chromatography.

9: ^1H NMR (CD_3CN) δ 5.48 (s, 5 H), 1.64 (three lines, $J_{\text{PH}+\text{PH}} = 6.6$ Hz, 36 H), -1.00 (quintet, $J_{\text{PH}} = 10.7$ Hz, 3 H); $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_3CN , -30°C) δ 104.1, 17.9 (quintet, $J_{\text{PC}} = 9$ Hz), -6.9 (br); ^{31}P NMR (CD_3CN) δ -42.1 ; IR (KBr) 1653 cm^{-1} . Anal. Calcd for $\text{C}_{18}\text{H}_{44}\text{NOP}_4\text{Re}$: C, 35.99; H, 7.38; N, 2.33. Found: C, 36.26; H, 7.68; N, 2.61.

A 1:1 mixture of **11** and **12:** ^1H NMR ($\text{THF-}d_8$, 47°C , 200 and 270 MHz) δ 6.74 (m, 1 H), 6.38 (m, 1 H), 6.28 (m, 1 H), 6.16 (m, 1 H), 6.06 (m, 1 H), 5.83 (m, 1 H), 2.90 (m, 4 H), 1.52 (d, $J_{\text{PH}} = 7$ Hz, 9 H), 1.51 (d, $J_{\text{PH}} = 7$ Hz, 9 H), 1.30 (two overlapping three-line patterns centered at 1.32 and 1.29, respectively, $J = 3$ Hz, 36 H), -0.97 (dt, $J = 13, 10$ Hz, 6 H); ^1H NMR ($\text{THF-}d_8$, -33°C); in addition to the resonances observed at 47°C , new resonances were seen at δ 6.34 (m) 6.21 (m), 5.95 (m), 5.75 (m), 5.15 (m), 2.99 (m), and 2.71 (m), the δ -0.97 resonance was observed as a complex set of overlapping multiplets (6 H); $^{13}\text{C}\{^1\text{H}\}$ NMR ($\text{THF-}d_8$, 0.09 M $\text{Cr}(\text{acac})_3$, -30°C) δ 173.3 (d, $J = 50$ Hz), 165.6 (d, $J = 45$ Hz), 151.3, 134.3, 131.5, 130.0, 128.6, 127.7, 57.0, 42.6, 20.0 (d, $J = 25$ Hz), 16.6 (t, $J = 12$ Hz), -4.1 , additional minor ^{13}C resonances were observed at δ 144.6, 135.4, 133.8, 127.0, 51.3, and -6.4 ; IR (THF) 1608 cm^{-1} . Anal. Calcd for $\text{C}_{15}\text{H}_{35}\text{NOP}_3\text{Re}$: C, 34.34; H, 6.72. Found: C, 34.08; H, 6.68. MS (26 eV) m/e calcd for $^{187}\text{Re-C}_{15}\text{H}_{35}\text{NOP}_3$ 525.1484, found 525.1492.

Synthesis of 9 from 3 and PMe_3 . When a THF solution of **3** (100 mg, 0.31 mmol) and PMe_3 (2 mL, 19.7 mmol, 4.0 M) was heated at 70°C for 29 h, yellow needles of **9** (16 mg, 8.7%) formed and were isolated by filtration. Evaporation of solvent gave a brown residue which was shown by ^1H NMR to be a mixture of 1.0 **8**:0.6 **11**:0.6 **12**:0.2 **6** and several minor impurities.

Conversion of 9 to 6. A sealed NMR tube containing solid **9** (9 mg, 0.015 mmol) and 0.28 mL of $\text{THF-}d_8$ was heated at 80°C for 96 h during which time **9** slowly dissolved and was cleanly converted to **6** and free PMe_3 as determined by ^1H NMR and IR.

Conversion of 11 and 12 to 6. A sealed NMR tube containing a benzene- d_6 solution of **11** and **12** (9 mg, 0.017 mmol, 0.08 M) was heated at 80°C for 24 h. ^1H NMR and IR indicated clean conversion to **6** and free PMe_3 .

X-ray Crystal Structure Determination of 9. Crystals of **9** suitable for X-ray diffraction study were obtained from a tetrahydrofuran- d_8 solution of **9**. A single crystal of approximate dimensions $0.05 \times 0.10 \times 0.30$ mm was mounted in a thin-walled glass capillary for the X-ray study. Preliminary examination of the crystal on a Syntex-Nicolet P1 diffractometer showed the crystal to be monoclinic. A Delaunay cell reduction did not reveal any hidden symmetry. The observed systematic absences of $h0l$ ($l = 2n + 1$) and $0k0$ ($k = 2n + 1$) uniquely define the space group as $P2_1/c$ (No. 14). The unit cell parameters, determined by a least-squares refinement utilizing the setting angles of 60 reflections ($2\theta < 41^\circ$) collected at $\pm 2\theta$, are $a = 12.893$ (2) \AA , $b = 13.622$ (2) \AA , $c = 15.068$ (2) \AA , and $\beta = 97.47$ (2) $^\circ$ (at $-90 \pm 5^\circ\text{C}$; $\lambda(\text{Mo K}\alpha) = 0.71073$ \AA). The unit cell volume of 2623.8 \AA^3 led to a calculated density of 1.52 g/cm^3 for 4 formula units of $\text{ReP}_4\text{NOCl}_8\text{H}_{44}$ per unit cell.

X-ray intensity data were collected at $-90 \pm 5^\circ\text{C}$ on a Syntex-Nicolet P1 diffractometer equipped with a graphite-monochromated Mo $\text{K}\alpha$ radiation source and a modified LT-1 low-temperature device. A total of 5967 unique reflections with $\sin \theta/\lambda \leq 0.649\text{ \AA}^{-1}$ were collected with use of a θ - 2θ step-scan technique with a scan range of 0.7° below $2\theta(\text{Mo K}\alpha_1)$ to 0.7° above $2\theta(\text{Mo K}\alpha_2)$ and a variable scan rate ($2.0\text{--}24.0^\circ/\text{min}$). Throughout data collection four standard reflections from diverse regions of reciprocal space were measured every 50 reflections. The intensities of the standard reflections showed no systematic variations during the time required to collect the data. The data were reduced and

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standard deviations calculated by using methods similar to those described previously.¹⁷ Absorption corrections were applied (empirical ψ -scan method, $\mu_{\text{Mo}} = 46.6 \text{ cm}^{-1}$). The minimum and maximum multipliers were 1.00 and 1.46, respectively.

The structure was solved by direct methods with use of the MULTAN¹⁸ package and the 300 reflections with the highest values of $|E|$. An E map based upon these reflections revealed positions for the rhenium atom and 8 of the other non-hydrogen atoms. Difference electron density maps revealed positions for the rest of the 25 non-hydrogen atoms. The model was refined by a full-matrix least-squares technique with use of the 4656 reflections with $F_o > 3\sigma(F_o)$ and standard atomic form factors.¹⁹ The effects of anomalous scattering for the rhenium and phosphorus atoms were included in the calculated structure amplitudes.²⁰ A difference electron density map calculated after refinement on the isotropic model had converged ($R_1 = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.108$; $R_2 = [\sum w(F_o - F_c)^2 / \sum w(F_o)^2]^{1/2} = 0.122$) demonstrated (nonstatistical) disorder of the nitrosyl and Re-bonded methyl group (the occupancies of 0.6 and 0.4 were estimated from the electron density difference map peaks from a

map calculated with the disordered atoms removed) and gave positions for the disordered atoms and for all the hydrogen atoms except those on the Re-bonded methyl group. The hydrogen atoms position and isotropic thermal parameters were included in the parameters being refined. All non-hydrogen atoms except the disordered nitrogen and carbon atoms were assumed to vibrate anisotropically. This final model converged with $R_1 = 0.025$ and $R_2 = 0.032$. The highest peak on the final difference electron density map was near the rhenium atom and was about 22% of the height of a typical carbon atom. The estimated error in an observation of unit weight was 1.15 and the final data to variable ratio was 11.7.

Acknowledgment. Support from the Department of Energy, Division of Basic Energy Sciences, is gratefully acknowledged. We thank Dr. Nicholas Vollendorf for first suggesting the structural assignments of **11** and **12**.

Registry No. **3**, 38814-45-8; **6**, 80668-22-0; **8**, 94729-27-8; **9**, 94619-90-6; **9-d**, 94619-92-8; **10**, 94619-86-0; **11**, 94619-87-1; **12**, 94619-88-2; PMe_3 , 594-09-2.

Supplementary Material Available: Listings of the final observed and calculated structure amplitudes ($\times 10$), atomic coordinates, and associated thermal parameters (24 pages). Ordering information is given on any current masthead page.

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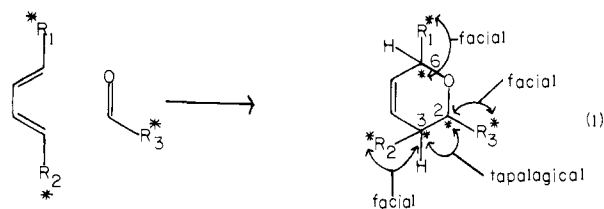
On the Scope, Mechanism, and Stereochemistry of the Lewis Acid Catalyzed Cyclocondensation of Activated Dienes with Aldehydes: An Application to the Erythronolide Problem

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Abstract: The scope of the titled reaction is described. Pericyclic and aldol-like pathways have been identified. To a great extent these are a function of the catalyst/solvent system and of structural features in the aldehyde. The pericyclic pathway tends to favor a topology leading to *cis*-2,3-dihydropyran. A complementary threo-selective siloxonium (aldol-like) pathway is favored by borontrifluoride catalysis. These capabilities are coordinated in a synthesis of the C_1 - C_9 fragment of 6a-deoxyerythronolide.

The ability of selected aldehydes bearing strongly electrophilic α -substituents to function as heterodienophiles (eq 1) has been



known for some time.¹⁻³ Even in these cases the substitution patterns of the diene participants have been quite simple. Therefore, extensive functional group manipulations would be required to convert the primary cycloadducts to more complex structures.

In such cycloaddition reactions, the issue of the relative configurations at positions 2 and 3 is one of topology. The emerging

relationship of both centers relative to preexisting dissymmetric elements in either the aldehyde (cf. R^*_3) or in the diene (cf. R^*_1 or R^*_2) falls under the category of diastereofacial selectivity.⁴

(1) For a recent comprehensive review of Diels-Alder cycloadditions with heterodienophiles, see: Weinreb, S. M.; Staib, R. R. *Tetrahedron* **1982**, *38*, 3087.

(2) For a very early foray into this area, see: Paul, R.; Ischelitcheff, S. *C. R. Hebd. Seances Acad. Sci.* **1947**, *224*, 1722. Recently, the use of ultrahigh pressure (~ 20 kbar) has extended the scope of reactivity of nonactivated carbonyl participants. See: Jurczak, J.; Chmielewski, M.; Filipek, S. *Synthesis* **1979**, 41.

(3) The possibility of employing Lewis acid catalysis in this type of cycloaddition was noted by J. W. Scheeren and associates in two publications which preceded our own.^{12a} However, these workers confined their reports to the case of activated aldehydes (cf. glyoxylate) which in fact do not require catalysis. Mention was made that Lewis acid catalysis could allow for the process to be extended to simple aldehydes but no examples were given. In a paper that appeared after our work,^{12b} the extension to unactivated aldehydes was described. Cf., inter alia: van Balen, H. C. J. G.; Broekhuis, A. A.; Scheeren, J. W.; Nivard, R. J. F., *Recl. Trav. Chim. Pays-Bas* **1979**, *98*, 36. Aben, R. W.; Scheeren, J. W. *J. Chem. Soc., Perkin Trans. 1* **1979**, 3132. Aben, R. W.; Scheeren, J. W. *Synthesis* **1982**, 779.

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