furthest downfield resonance(s) for η^5-2,4-dimethylpentadienyl ligands,[16] one can observe that one resonance is even further downfield—this may readily be assigned to the two terminal hydrogen atoms on the C_7H_9 ligand. By -50 °C, one observes a 1:1:1:1:1:1:3:3:3:3:1:1 pattern,[17] consistent with the placement of both organic ligands in unsymmetric environments, such as in the observed structure. On the basis of this structure, one would expect that rotation of the C_7H_{11} ligand alone should restore the spectral symmetry. In accord with this, the values of ΔG^* for all five pairs of resonances are essentially identical at 12.6 ± 0.15 kcal/mol.[18] This value is quite similar to those observed in a variety of both mono(pentadienyl)- and bis(pentadienyl)metal complexes.[16,19]

In general, the loss of hydrogen substituents from terminal pentadienyl ligand sites should be expected to provide for some interesting conversions, as metallacyclohexadiene,[20] metallabenzene,[21] and cyclopentadienyl[22] complexes could easily result.[23] In fact, mass spectra of some "half-open metallocenes" show prominent peaks corresponding to loss of H_2, while some "open metallocenes" show prominent peaks corresponding to loss of $2H_2$.[24] It can easily be envisioned that these H_2 losses are accompanied by the conversion of pentadienyl to cyclopentadienyl ligands. In another example, the attempted preparation of a (pentadienyl)iridium compound led instead to a (hydrido)iridacyclohexadiene complex, $HIr(C_7H_{10})(PEt_3)_3$, which could be converted to a cyclopentadienyl complex following hydride abstraction.[20b] However, metallabenzene complexes have to date not been isolated from pentadienyl complexes and are rather rare species that may themselves be readily converted to cyclopentadienyl complexes.[21,22] In the present case, the survival of the metallabenzene unit may be dependent on the fact it is η^6-bound to the Mo(1) atom, and while one might expect a reductive elimination to lead to a cyclopentadienyl complex, we have not yet observed such a transformation to take place. For example, addition of phosphine or phosphite ligands seems to bring about CO substitution instead.[25] Further studies designed to probe the reaction chemistry of this unusual system are in progress.

Acknowledgment. R.D.E. is grateful to the National Science Foundation for generous support of this research.

Supplementary Material Available: Synthetic, spectroscopic, and analytical details for all new compounds, as well as a complete description of the crystallographic study, including tables of atomic parameters and pertinent bond distances and angles (17 pages); the structure factor tables (21 pages). Ordering information is given on any current masthead page.

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[16] (a) Wilson, D. R.; DiLullo, A. A.; Ernst, R. D. *J. Am. Chem. Soc.* **1980**, *102*, 5928. (b) Liu, J.-Z.; Ernst, R. D. *Ibid.* **1982**, *104*, 3737. (c) Wilson, D. R.; Ernst, R. D.; Cymbaluk, T. H. *Organometallics* **1983**, *2*, 1220.

[17] NMR (^{1}H, toluene-d_8, −80 °C): δ 8.31 (s, 1 H), 6.91 (s, 1 H), 5.74 (s, 1 H), 4.11 (s, 1 H), 2.31 (s, 1 H), 2.20 (s, 1 H), 1.84 (s, 3 H), 1.79 (s, 3 H), 1.47 (s, 3 H), 0.61 (s, 3 H), 0.28 (s, 1 H), 0.16 (s, 1 H). The underlined resonances are those which do not undergo exchange processes since they are located on the central carbon atoms. Note that one of these shows a strong temperature dependence. NMR (^{13}C, toluene-d_8, −80 °C): δ 228.1 (s, 1 C), 226.2 (br s, 3 C), 220.2 (s, 1 C), 165.9 (d, 1 C, J = 141 Hz), 154.5 (d, 1 C, J = 142 Hz), 117.5 (s, 1 C), 111.4 (s, 1 C), 110.8 (s, 1 C), 108.0 (s, 1 C), 103.3 (d, 1 C, J = 160 Hz), 97.0 (d, 1 C, J = 161 Hz), 65.9 (t, 1 C, J = 156 Hz), 55.9 (t, 1 C, J = 159 Hz), 28.9 (q, 1 C, J = 126 Hz), 28.4 (q, 1 C, J = 127 Hz), 28.0 (q, 1 C, J = 127 Hz), 25.2 (q, 1 C, J = 126 Hz). The large downfield shifts for two of the CH resonances (at 165.9 and 154.5 ppm) indicate that these arise from the terminal carbon atoms of the C_7H_9 ligand.

[18] (a) It can be noted that every higher temperature resonance which decoalesces leads to two adjacent resonances at low temperatures; i.e., the frequency separations happen to be small enough that no other resonance falls between them. For the five pairs of low-temperature resonances, the frequency separations (Hz) and coalescence temperatures, from low to high field, are (420.2, 9 °C), (33.3, −20°), (14.5, −28 °C), (259.0, 0 °C), and (34.4, −18 °C), corresponding to ΔG^* values (±0.3 kcal/mol) of 12.6, 12.6, 12.6, 12.5, and 12.7 kcal/mol, respectively. (b) ΔG^* (J/mol) = 19.13 $(T_c)(9.97 + \log T_c/\delta\nu)$.[17c] (c) Günther, H. *NMR Spectroscopy*; Wiley: New York, 1980; p 243.

[19] (a) Stahl, L.; Ernst, R. D. *Organometallics* **1983**, *2*, 1229. (b) Bleeke, J. R.; Stanley, G. G.; Kotyk, J. J. *Ibid.* **1986**, *5*, 1642. (c) Whitesides, T. H.; Budnik, R. A. *Inorg. Chem.* **1975**, *14*, 664.

[20] (a) Grabowski, N. A.; Hughes, R. P.; Jaynes, B. S.; Rheingold, A. L. *J. Chem. Soc., Chem. Commun.* **1986**, 1694. (b) Bleeke, J. R.; Peng, W.-J. *Organometallics* **1987**, *6*, 1576. (c) Egan, J. W., Jr.; Hughes, R. P.; Rheingold, A. L. *Ibid.* **1987**, *6*, 1578.

[21] Elliot, G. P.; Roper, W. R.; Waters, J. M. *J. Chem. Soc., Chem. Commun.* **1982**, 811.

[22] (a) Ferede, R.; Allison, N. T. *Organometallics* **1983**, *2*, 463. (b) See also: Pedersen, S. F.; Schrock, R. R.; Churchill, M. R.; Wasserman, H. J. *J. Am. Chem. Soc.* **1982**, *104*, 6808.

[23] As the observed product formally results from the loss of C_2H_4, H_2, CO, and 2KI from the starting materials, one might readily speculate on the other products formed during the reaction. Spectral examination of the gaseous hydrocarbon product revealed the presence of ethylene and the absence of ethane. At this stage a mechanism for the metallabenzene complex formation can only be speculated. Actually, a number of possible pathways could be followed. If a complex having two $Mo(C_7H_{11})(CO)_3$ units bridged by C_2H_4 is initially formed, an η^5–η^3 pentadienyl conversion could be followed by an oxidative addition of a terminal C–H bond to the 16-electron molybdenum center. β-elimination of either molybdenum unit to the other, accompanied by either an η^5–η^3 or η^3–η^1 ligand conversion, could lead to an ethylene complex, after which the ethylene could be lost. Subsequent steps involving oxidative additions of Mo–C and C–H bonds to molybdenum centers could ultimately lead to the observed product (with elimination of H_2 and CO). One of the many other alternatives involves CO loss occurring as a first step, followed by steps similar to those described above. Future labeling studies should partially help to understand the process by which the complex was formed.

[24] (a) The abundance of such ions is very dependent on the ionizing potential, but nonetheless such peaks are quite significant in species such as $V[1,5\text{-}(SiMe_3)_2C_5H_5]_2$, $V(C_5H_5)[1,5\text{-}(SiMe_3)_2C_5H_5]$, $Cr(2,4\text{-}C_7H_{11})_2$, and $Cr(C_5Me_5)(C_5H_7)$, as well as a wide variety of other related complexes.[24b] (b) Freeman, J. W.; Gedridge, R. W.; Ernst, R. D., unpublished results.

[25] Kralik, M. S.; Ernst, R. D., unpublished results.

Synthesis and First Structural Characterization of Transition-Metal Complexes Containing η^1-*cis*-Pentadienyl and η^1-*trans*-Pentadienyl Ligands[1]

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Summary: Reaction of (η^5-pentadienyl)Re(CO)$_3$ with PEt$_3$ in refluxing diethyl ether produces (*fac*-η^1-*cis*-pentadienyl)Re(CO)$_3$(PEt$_3$)$_2$ (**1a**), which slowly converts to its η^1-*trans*-pentadienyl isomer, **1b**. Analogous products, **2a** and **2b**, are produced under similar conditions in the PMe$_3$ system. When **2** is reacted with additional PMe$_3$ in refluxing *tetrahydrofuran*, carbonyl substitution occurs and (*mer*-η^1-*trans*-pentadienyl)Re(CO)$_2$(PMe$_3$)$_3$ (**3**) is produced. Both **1a** and **3** have been structurally characterized.

During the past several years, there has been increasing interest in the synthesis and reactivity of pentadienyl–transition-metal complexes.[2] One reason for this interest

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[1] Pentadienyl-Metal-Phosphine Chemistry. 14. For the previous two papers in this series, see: (a) Bleeke, J. R.; Donaldson, A. J.; Peng, W.-J. *Organometallics* 1987, *6*, xxxx. (b) Bleeke, J. R.; Peng, W.-J. *Ibid.* 1987, *6*, 1576.

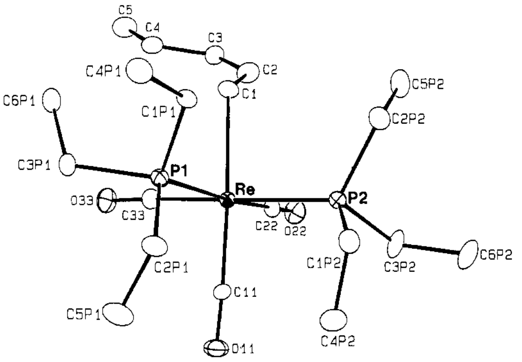
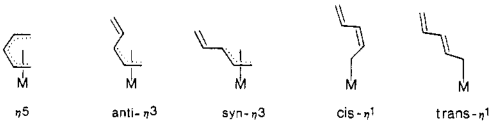


Figure 1. ORTEP drawing of (*fac*-η^1-*cis*-pentadienyl)Re(CO)$_3$(PEt$_3$)$_2$ (**1a**). Bond distances and angles: Re–P1, 2.409 (3) Å; Re–P2, 2.506 (3) Å; Re–C11, 1.92 (1) Å; Re–C22, 1.94 (1) Å; Re–C33, 1.92 (1) Å; Re–C1, 2.31 (1) Å; C1–C2, 1.47 (2) Å; C2–C3, 1.36 (2) Å; C3–C4, 1.42 (2) Å; C4–C5, 1.37 (2) Å; P1–Re–P2, 94.3 (1)°; P1–Re–C11, 94.7 (4)°; P1–Re–C22, 175.0 (4)°; P1–Re–C33, 88.5 (4)°; P1–Re–C1, 86.0 (3)°; P2–Re–C11, 91.2 (3)°; P2–Re–C22, 87.8 (3)°; P2–Re–C33, 177.0 (4)°; P2–Re–C1, 92.2 (3)°; C11–Re–C22, 89.7 (5)°; C11–Re–C33, 89.5 (5)°; C11–Re–C1, 176.5 (5)°; C22–Re–C33, 89.4 (5)°; C22–Re–C1, 89.4 (4)°; C33–Re–C1, 87.0 (5)°; Re–C1–C2, 114.0 (8)°; C1–C2–C3, 130 (1)°; C2–C3–C4, 126 (1)°; C3–C4–C5, 123 (1)°.

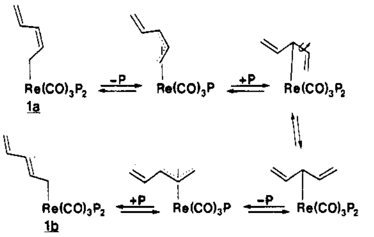
is the flexibility of the pentadienyl ligand—its ability to assume bonding modes with a variety of geometries and hapticities. Although a substantial number of transition metal complexes containing pentadienyl ligands in the syn-η^3, anti-η^3, and η^5-bonding modes have been synthesized and structurally characterized, η^1-pentadienyl metal complexes are still rather rare,[3,4] and, until now, none have been structurally characterized.[5] We report herein the syntheses and first X-ray crystal structures of transition-metal complexes containing η^1-*cis*-pentadienyl and η^1-*trans*-pentadienyl ligands.



Several years ago, Powell[6] demonstrated that (η^5-pentadienyl)Mn(CO)$_3$ reacts with trialkylphosphines, PR$_3$, to produce mono(phosphine) adducts, (η^3-pentadienyl)Mn(CO)$_3$(PR$_3$). We now report that (η^5-pentadienyl)Re(CO)$_3$[7] reacts cleanly with 2 equiv of triethylphosphine in refluxing diethyl ether to yield the bis(phosphine) adduct (*fac*-η^1-*cis*-pentadienyl)Re(CO)$_3$(PEt$_3$)$_2$ (**1a**).[8,9] An ORTEP drawing of the molecular structure of **1a**, derived from a single-crystal X-ray diffraction study,[10] is shown in Figure 1.

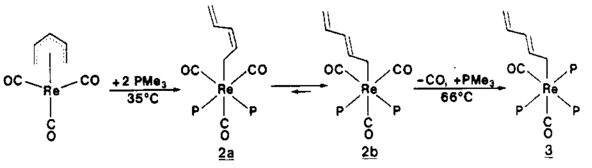
The three carbonyl ligands in **1a** are oriented in a facial geometry, with one carbonyl situated trans to the penta-

Scheme I[a]



[a] P = PEt$_3$.

Scheme II[a]



[a] P = PMe$_3$.

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(2) (a) Ernst, R. D. *Acc. Chem. Res.* **1985**, *18*, 56. (b) Yasuda, H.; Nakamura, A. *J. Organomet. Chem.* **1985**, *285*, 15. (c) Powell, P. *Adv. Organomet. Chem.* **1986**, *26*, 125. (d) Yasuda, H.; Tatsumi, K.; Nakamura, A. In *Recent Advances in Anionic Polymerization*; Hogen-Esch, T. E., Smid, J., Eds.; Elsevier: Lausanne, 1987; p 59.

(3) The following papers contain reports of (η^1-pentadienyl)metal complexes: (a) Yasuda, Y.; Nagasuma, K.; Akita, M.; Lee, K.; Nakamura, A. *Organometallics* **1984**, *3*, 1470. (b) Lush, S.-F.; Liu, R.-S. *Ibid.* **1986**, *5*, 1908. (c) Lee, G.-H.; Peng, S.-M.; Lee, T.-W.; Liu, R.-S. *Ibid.* **1986**, *5*, 2378. (d) Lee, T.-W.; Liu, R.-S. *J. Organomet. Chem.* **1987**, *320*, 211.

(4) (η^1-Pentadienyl)metal complexes have also been postulated as intermediates in *anti*-η^3- to *syn*-η^3-pentadienyl ligand isomerization processes: (a) Bleeke, J. R.; Peng, W.-J. *Organometallics* **1984**, *3*, 1422. (b) Bleeke, J. R.; Kotyk, J. J. *Ibid.* **1985**, *4*, 194.

(5) Structures of several η^1-pentadienyl complexes involving main-group metals have been reported: (a) Yasuda, H.; Yamauchi, M.; Nakamura, A.; Sei, T.; Kai, Y.; Yasuoka, N.; Kasai, N. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 1089. (b) Yasuda, H.; Ohnuma, Y.; Nakamura, A.; Kai, Y.; Yasuoka, N.; Kasai, N. *Ibid.* **1980**, *53*, 1101.

(6) Paz-Sandoval, M. A.; Powell, P.; Drew, M. G. B.; Perutz, R. N. *Organometallics* **1984**, *3*, 1026.

(7) Paz-Sandoval, M. A.; Powell, P. *J. Organomet. Chem.* **1981**, *219*, 81.

(8) **Synthesis of (*fac*-η^1-*cis*-Pentadienyl)Re(CO)$_3$(PEt$_3$)$_2$ (1a).** In a typical reaction, a solution containing 1.0 g (3.0 × 10^{-3} mol) of (η^5-C$_5$H$_7$)Re(CO)$_3$, 1.05 g (9.0 × 10^{-3} mol) of PEt$_3$, and 50 mL of diethyl ether was refluxed for 12 h under N$_2$. After filtering, the pale amber solution was concentrated to 15 mL and cooled to −30 °C, causing **1a** to crystallize: yield of crude product, 1.5 g (85%); yield of crystalline product, 0.8 g (45%). Anal. Calcd for $ReP_2O_3C_{20}H_{37}$: C, 41.87; H, 6.50. Found: C, 41.62; H, 6.43.

Spectroscopic Data for 1a. ^{1}H NMR (benzene-d_6, 20 °C, 300 MHz): δ 7.32 (d of t, J_{H-H5_a} = 17.1 Hz, $J_{H-H3/H5_s}$ = 10.6 Hz, 1, H4), 6.51 (pseudo q, $J_{H-H1/H3}$ = 9.8 Hz, 1, H2), 5.84 (d of d, H_{H-H4} = 10.6 Hz, J_{H-H2} = 9.8 Hz, 1, H3), 5.19 (d of d, J_{H-H4} = 17.1 Hz, J_{H-H5_s} = 2.5 Hz, 1, H5$_a$), 5.06 (br d, J_{H-H4} = 10.6 Hz, 1, H5$_s$), 1.76 (pseudo q, $J_{H-H2/P}$ = 9.8 Hz, 2, H1's), 1.51 (m, 12, phosphine CH$_2$'s), 0.78 (m, 18, phosphine CH$_3$'s). ^{13}C{^{1}H} NMR (benzene-d_6, 20 °C, 75 MHz): δ 195.3 (m, CO's trans to P's), 192.6 (t, J_{C-P} = 8.3 Hz, CO trans to pentadienyl), 148.9 (s, C2), 134.4 (s, C4), 116.9 (s, C3), 110.4 (s, C5), 19.9 (virtual t, J_{C-P} = 26.5 Hz, phosphine CH$_2$'s), 8.31 (s, phosphine CH$_3$'s), −3.9 (t, J_{C-P} = 7.7 Hz, C1). ^{31}P{^{1}H} NMR (benzene-d_6, 20 °C, 121 MHz, referenced to H$_3$PO$_4$): δ −16.7 (s). IR (benzene, 20 °C, selected peaks): 2008, 1922, 1881 cm^{-1} (vs, C≡O stretches); 1610, 1605 cm^{-1} (s, C═C stretches); 1010 cm^{-1} (vs, P—C stretch).

(9) This reaction is closely related to the reaction of (η^5-cyclopentadienyl)Re(CO)$_3$ with PMe$_3$, which produces (*fac*-η^1-cyclopentadienyl)Re(CO)$_3$(PMe$_3$)$_2$: Casey, C. P.; O'Connor, J. M.; Jones, W. D.; Haller, K. J. *Organometallics* **1983**, *2*, 535.

(10) Crystals of **1a** were triclinic, space group $P\bar{1}$ (No. 2) with a = 8.907 (3) Å, b = 17.055 (8) Å, c = 8.212 (4) Å, α = 93.39 (4)°, β = 103.85 (4)°, γ = 86.57 (3)°, V = 1208 (1) Å^3, Z = 2, and d_{calcd} = 1.58 g/cm^3.

A pale amber single crystal of dimensions 0.2 mm × 0.2 mm × 0.3 mm was grown from a saturated diethyl ether solution and sealed in a glass capillary under an inert atmosphere. X-ray diffraction data were collected at 22 °C on a Nicolet P3 diffractometer using graphite-monochromated Mo Kα radiation. A total of 4248 independent reflections with 4° < 2θ < 50° were collected by using the ω-scanning technique and a variable scan rate of 3–23°/min. (A rapid scan rate was employed due to persistent problems with decay.) All of the data reduction and structure refinement were done with a modified Enraf-Nonius Structure Determination Package (modified by B.A. Frenz and Assoc., Inc., College Station, TX) on a VAX 11/780 computer. The data were corrected for Lorentz and polarization effects, for linear decay (23.1%), and for absorption/extinction using program DIFABS (μ = 52.44 cm^{-1}). Only the 2776 independent reflections with intensities greater than 3 times their estimated standard deviations were used in the least-squares refinements. The structure was solved by standard Fourier techniques following the location of the Re atom from a Patterson map. All non-hydrogens were refined anisotropically. Hydrogen atoms were placed at idealized positions riding upon their respective carbon atoms and included in the structure factor calculations, but not refined. The isotropic thermal parameter of each hydrogen atom was fixed at 1.2 times the equivalent isotropic thermal parameter of the carbon atom to which it is covalently bonded. The convergence values of the agreement indices were R_F = 0.040 and R_{wF} = 0.044.

dienyl group and the other two trans to PEt_3 ligands. The pentadienyl group is bonded to rhenium through C1 and retains cis geometry about its internal double bond (C2–C3). Its sickle shape is reflected in torsional angles of 3.4° and 178.20° for C1–C2–C3–C4 and C2–C3–C4–C5, respectively. The five pentadienyl carbon atoms are coplanar to within 0.01 Å, and the pentadienyl plane makes a dihedral angle of 28.8° with the equatorial plane (Re/P1/P2/C22/C33). Pentadienyl vector C1–C2 approximately eclipses carbonyl ligand C22–O22; plane Re/C1/C2 intersects plane C1/Re/C22 with a dihedral angle of 11.9°. The expected alternation is observed in the pentadienyl C–C bond lengths: C1–C2 = 1.47 (2) Å; C2–C3 = 1.36 (2) Å; C3–C4 = 1.42 (2) Å; C4–C5 = 1.37 (2) Å.

Characteristic of the cis geometry about the internal double bond, C2–C3, is the relatively small coupling constant between H2 and H3 (9.8 Hz). A second distinguishing feature of the ^1H NMR spectrum of **1a** is the downfield shift of H4's signal relative to that of H2 (δ 7.32 vs δ 6.51).

When **1a** is stirred in diethyl ether at 25 °C, the pentadienyl ligand slowly isomerizes from cis geometry to trans. After 2 weeks at 25 °C, the isomerization to (*fac*-η^1-*trans*-pentadienyl)$Re(CO)_3(PEt_3)_2$ (**1b**) is 95% complete.[11] In the trans isomer, J_{H2-H3} is 14.4 Hz and the ^1H NMR signal for H4 overlaps with that for H2 (δ 6.75–6.71).[12] We believe that this slow isomerization proceeds through the intermediacy of η^3-pentadienyl and C3-bound η^1-pentadienyl species, as shown in Scheme I below. Compound **1** does not react with additional triethylphosphine in refluxing diethyl ether or tetrahydrofuran.[13]

The reaction of (η^5-pentadienyl)$Re(CO)_3$ with trimethylphosphine in refluxing diethyl ether proceeds cleanly to give the PMe_3 analogue of **1**, (*fac*-η^1-pentadienyl)$Re(CO)_3(PMe_3)_2$ (**2**).[9,14] The kinetic product is again the η^1-*cis*-pentadienyl isomer, and this species slowly isomerizes to the η^1-*trans*-pentadienyl isomer. However, in contrast to **1**, **2** reacts with additional phosphine in refluxing *tetrahydrofuran*; one of the carbonyl ligands is replaced by a trimethylphosphine ligand, yielding (*mer*-η^1-*trans*-pentadienyl)$Re(CO)_2(PMe_3)_3$ (**3**)[15] (see Scheme II).

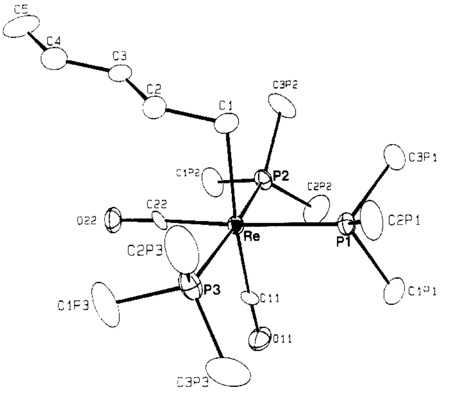

Figure 2. ORTEP drawing of (*mer*-η^1-*trans*-pentadienyl)Re-$(CO)_2(PMe_3)_3$ (**3**). Bond distances and angles: Re–P1, 2.470 (4) Å; Re–P2, 2.395 (4) Å; Re–P3, 2.399 (5) Å; Re–C11, 1.89 (2) Å; Re–C22, 1.88 (1) Å; Re–C1, 2.34 (2) Å; C1–C2, 1.51 (3) Å; C2–C3, 1.27 (2) Å; C3–C4, 1.39 (2) Å, C4–C5, 1.29 (2) Å; P1–Re–P2, 93.1 (2)°; P1–Re–P3, 93.0 (2)°; P1–Re–C11, 91.3 (4)°; P1–Re–C22, 176.5 (5)°; P1–Re–C1, 84.2 (5)°; P2–Re–P3, 173.6 (2)°; P2–Re–C11, 88.0 (5)°; P2–Re–C22, 85.3 (5)°; P2–Re–C1, 90.0 (6)°; P3–Re–C11, 89.9 (5)°; P3–Re–C22, 88.7 (5)°; P3–Re–C1, 92.5 (6)°; C11–Re–C22, 91.7 (7)°; C11–Re–C1, 175.0 (7)°; C22–Re–C1, 92.7 (6)°; Re–C1–C2, 108 (1)°; C1–C2–C3, 130 (3)°; C2–C3–C4, 132 (3)°; C3–C4–C5, 135 (3)°.

An ORTEP drawing of the X-ray crystal structure of **3** is shown in Figure 2.[16]

In **3**, one of the two remaining carbonyl ligands resides trans to the η^1-pentadienyl group, while the other carbonyl lies trans to a phosphine. The η^1-pentadienyl group is bonded to rhenium through C1 and has a trans geometry about internal double bond C2–C3. Its W-shape gives rise to torsional angles of 178.2° and 177.8° for C1–C2–C3–C4

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(11) **Synthesis of (*fac*-η^1-*trans*-Pentadienyl)$Re(CO)_3(PEt_3)_2$ (1b).** A solution containing 0.25 g (4.3×10^{-4} mol) of **1a** in 10 mL of diethyl ether was stirred for 3 weeks at 25 °C. The pale amber solution was then concentrated and cooled to −30 °C, causing **1b** to precipitate; yield of crude product, 0.22 g (90%). Anal. Calcd for $ReP_2O_3C_{20}H_{37}$: C, 41.87; H, 6.50. Found: C, 41.60; H, 6.40.

Spectroscopic Data for 1b. ^1H NMR (benzene-d_6, 20 °C, 300 MHz): δ 6.75–6.71 (m, 2, H2, H4), 6.10 (d of d, $J_{H-H2} = 14.4$ Hz, $J_{H-H4} = 10.3$ Hz, 1, H3), 5.04 (d of d, $J_{H-H4} = 16.6$ Hz, $J_{H-H5_s} = 2.0$ Hz, 1, $H5_a$), 4.79 (d of d, $J_{H-H4} = 11.2$ Hz, $J_{H-H5_a} = 2.0$ Hz, 1, $H5_s$), 1.61 (m, 2, H1's), 1.52 (m, 12, phosphine CH_2's), 0.80 (m, 18, phosphine CH_3's). $^{13}C\{^1H\}$ NMR (benzene-d_6, 20 °C, 75 MHz): δ 195.5 (m, CO's trans to P's), 192.8 (t, $J_{C-P} = 7.2$ Hz, CO trans to pentadienyl), 152.2 (s, C2), 139.6 (s, C4), 119.7 (s, C3), 107.6 (s, C5), 19.6 (virtual t, $J_{C-P} = 26.7$ Hz, phosphine CH_2's), 8.1 (s, phosphine CH_3's), 0.61 (t, $J_{C-P} = 7.6$ Hz, C1). $^{31}P\{^1H\}$ NMR (benzene-d_6, 20 °C, 121 MHz, referenced to H_3PO_4): δ −16.4 (s). IR (benzene, 20 °C, selected peaks): 2005, 1905, 1880 cm^{-1} (vs, C≡O stretches); 1618, 1610 cm^{-1} (s, C=C stretches); 1010 cm^{-1} (P—C stretch).

(12) The *fac* geometry is retained, as evidenced by the second-order AA′XX′ ^{13}C NMR signal exhibited by the CO ligands *trans* to PEt_3 ligands: Emsley, J. W.; Feeney, J.; Sutcliffe, L. H. *High Resolution Nuclear Magnetic Resonance Spectroscopy*; Pergamon: New York, 1966; pp 392–399.

(13) However, upon prolonged heating in diethyl ether, **1** is converted to a new, unidentified complex.

(14) Spectroscopic data for (*fac*-η^1-*cis*-pentadienyl)$Re(CO)_3(PMe_3)_2$ (**2a**) and (*fac*-η^1-*trans*-pentadienyl)$Re(CO)_3(PMe_3)_2$ (**2b**) are very similar to those reported in footnotes 8 and 11 for **1a** and **1b**. A complete set of NMR data is included in supplementary material.

(15) **Synthesis of (*mer*-η^1-*trans*-Pentadienyl)$Re(CO)_2(PMe_3)_3$ (3).** A solution containing 1.0 g (3.0×10^{-3} mol) of (η^5-C_5H_7)$Re(CO)_3$, 1.1 g (1.4×10^{-2} mol) PMe_3, and 50 mL of tetrahydrofuran was refluxed for 12 h under N_2. The solution was then evaporated to dryness, and the off-white residue was extracted with 30 mL of diethyl ether. After filtering, the pale amber solution was concentrated to 15 mL and cooled to −30 °C, causing **3** to crystallize: yield of crude product, 1.5 g (90%); yield of crystalline product, 0.8 g (50%). Anal. Calcd for $ReP_3O_2C_{16}H_{34}$: C, 35.75; H, 6.38. Found: C, 35.47; H, 6.30.

Spectroscopic Data for 3. ^1H NMR (benzene-d_6, 20 °C, 300 MHz): δ 6.74 (m, 1, H4), 6.62 (d of t, $J_{H-H3} = 14.6$ Hz, $J_{H-H1} = 9.0$ Hz, 1, H2), 5.89 (d of d, $J_{H-H2} = 14.6$ Hz, $J_{H-H4} = 10.8$ Hz, 1, H3), 5.07 (d of d, $J_{H-H4} = 17.4$ Hz, $J_{H-H5_s} = 2.2$ Hz, 1, $H5_a$), 4.79 (d of d, $J_{H-H4} = 9.6$ Hz, $J_{H-H5_a} = 2.2$ Hz, 1, $H5_s$), 1.45 (complex m, 2, H1's), 1.29 (complex m, 18, CH_3's of mutually trans phosphines), 0.96 (br d, $J_{H-P} = 6.9$ Hz, 9, CH_3's of phosphine trans to CO). $^{13}C\{^1H\}$ NMR (benzene-d_6, 20 °C, 75 MHz): δ 201.3 (d of t, $J_{C-P} = 56$ Hz, $J_{C-P} = 9.2$ Hz, CO trans to P), 197.5 (q, $J_{C-P} = 8.0$ Hz, CO trans to pentadienyl), 154.0 (s, C2), 140.1 (s, C4), 118.2 (s, C3), 106.0 (s, C5), 20.6 (virtual t, $J_{C-P} = 28$ Hz, CH_3's of mutually trans phosphines), 19.7 (d of t, $J_{C-P} = 25$ Hz, $J_{C-P} = 3.2$ Hz, CH_3's of phosphine trans to CO), 6.5 (q, $J_{C-P} = 7.2$ Hz, C1). $^{31}P\{^1H\}$ NMR (benzene-d_6, 20 °C, 121 MHz, referenced to H_3PO_4): δ −42.9 (d, $J_{P-P} = 27.7$ Hz, 2, mutually trans P's), −45.2 (t, $J_{P-P} = 27.7$ Hz, 1, P trans to CO). IR (benzene, 20 °C, selected peaks): 1922, 1837 cm^{-1} (vs, C≡O stretches); 1618 cm^{-1} (vs, C=C stretch); 950 cm^{-1} (vs, P—C stretch).

(16) Crystals of **3** were orthorhombic, space group $Pna2_1$ (No. 33), with $a = 13.869$ (4) Å, $b = 16.332$ (6) Å, $c = 10.268$ (2) Å, $V = 2325$ (2) Å^3, $Z = 4$, and $d_{calcd} = 1.54$ g/cm^3. Data were obtained at 22 °C on a pale amber single crystal of dimensions 0.3 mm × 0.3 mm × 0.4 mm using the diffractometer described in footnote 10. A total of 2372 independent reflections with $4° < 2\theta < 50°$ were collected by using the ω scanning technique and a variable scan rate of 3–23°/min. Data reduction, including a linear decay correction (5.1%) and an empirical absorption/extinction correction ($\mu = 55.03$ cm^{-1}), was carried out as described in footnote 10. Only the 1496 reflections with $I > 3\sigma(I)$ were used in the least-squares refinements. The structure was solved by standard Fourier techniques following the location of the rhenium atom from a Patterson map. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were treated as described in footnote 10. The convergence values of the agreement indices were $R_F = 0.028$ and $R_{wF} = 0.041$. Note: The absolute structure of the complex was tested prior to the application of DIFABS by inverting the signs of the non-hydrogen atom coordinates and re-refining the structure. The resulting agreement indices were significantly higher than those for the structure reported.

and C2–C3–C4–C5, respectively. The five pentadienyl carbon atoms are coplanar to within 0.01 Å and the pentadienyl plane makes a dihedral angle of 28.9° with the equatorial plane Re/P1/P2/P3/C22. The projection of pentadienyl vector C1–C2 onto the equatorial plane falls between carbonyl ligand C22–O22 and phosphine ligand P3; plane Re/C1/C2 makes a dihedral angle of 23.3° with plane C1/Re/C22. A clear alternation in pentadienyl C–C bond lengths is again observed: C1–C2 = 1.51 (3) Å; C2–C3 = 1.27 (2) Å; C3–C4 = 1.39 (2) Å; C4–C5 = 1.29 (2) Å.

In solution, the η^1-*trans*-pentadienyl ligand in **3** gives rise to a ^{1}H NMR spectrum that closely resembles those of **1b** and **2b**. Particularly diagnostic are the large J_{H2-H3} coupling constant (14.6 Hz) and the upfield chemical shift of H4 (δ 6.74), which is comparable to that of H2.

We have begun to study the reactivity of these unusual (η^1-pentadienyl)rhenium complexes toward heat, light, and electrophilic reagents. Results of these investigations will be reported in future communications.

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Supplementary Material Available: Synthesis and spectroscopic characterization of **2** and listings of final atomic coordinates, thermal parameters, bond lengths, bond angles, torsional angles, and significant least-squares planes including subtended dihedral angles for **1a** and **3** (16 pages); listings of observed and calculated structure factor amplitudes for **1a** and **3** (17 pages). Ordering information is given on any current masthead page.

Spectroscopic Observation of Silylene–Ether Complexes

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Summary: The ultraviolet photolysis of linear trisilanes in 2-MeTHF at 77 K has led to the first spectroscopic detection of silylene ether complexes. The complexes are also formed during the annealing of mixed 3-MP/2-MeTHF glasses. Chemical evidence for complexed silylenes based on competitive trapping studies as well as evidence that the silylene–ether complexes have a significant lifetime in solution at low temperatures is presented.

The isolation of silylenes in argon or hydrocarbon matrices has in recent years contributed greatly to the knowledge of these reactive species.[1,2] Here we report the results of recent investigations of diorganosilylenes in pure 2-methyltetrahydrofuran (2-MeTHF) glasses and in 3-methylpentane (3-MP) matrices containing ether dopants, leading to the first spectroscopic observation of silylene–ether complexes.

Table I. Absorption Maxima for Silylenes and Their Annealing Products in 2-MeTHF and 3-MP Matrices at 77 K

		2-MeTHF		3-MP	
R	R′	λ_{max}	annealed λ_{max}	λ_{max}	annealed λ_{max}
Mes	*t*-Bu	510, 350	350	505	335, 390
Mes	OAr	430	330	425	350, 390, 430
Mes	Ad	526, 530	350	526	338, 392
Mes	Mes	350	350	577	420

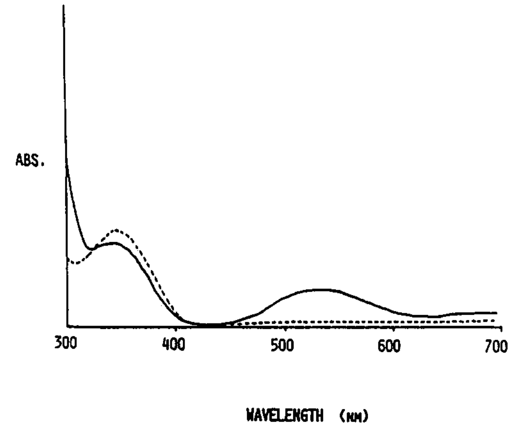

Figure 1. UV spectrum obtained in photolysis of **1c** in 2-MeTHF at 77K (—). Spectrum observed after annealing of the matrix (- - -).

Ether-stabilized silylenes were first proposed as intermediates by Weber and Steele in 1980.[3] In these studies dimethylsilylene was observed to react with increased selectivity in ether solvents leading the authors to postulate an "electron-pair donor complex with the solvent"[3] as the cause of the observed selectivity. Silylene complexes with Lewis bases have also been proposed on theoretical grounds.[4] However, no spectroscopic evidence for such complexes has been reported.[5]

In our experiments, trisilanes **1a–d** were photolyzed to give the corresponding silylenes.[6] In 3-MP at 77 K compounds **1a–d** behave similarly to other trisilanes whose photolyses have been studied earlier.[2] Initially, absorption bands due to the silylene are observed; upon annealing of the matrix these disappear and bands of the disilene appear (Table I). For **1a,c,d** the disilenes are stable and can be isolated.

When a similar photolysis of **1a** or **1c** was carried out in a matrix composed of 95:5 3-MP/2-MeTHF, initially only bands due to the silylene were observed, but upon annealing these disappeared and a new band was formed with λ_{max} = 350 nm. After further warming, this band diminished and the band associated with the disilene grew in. The disilene was stable to room temperature and was detected by GC–MS as the 1,3-cyclodisiloxane following the addition of O_2 to the solution.[7]

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(1) Gaspar, P. P. In *Reactive Intermediates*; Jones, M., Ed.; Wiley, New York, 1985; Vol. 3, p 333.

(2) Michalczyk, M. J.; Fink, M. J.; De Young, D. J.; Carlson, C. W.; Welsh, K. M.; West, R. *Silicon, Germanium, Tin Lead Compds.* **1986**, *1*, 75–80.

(3) Steele, K. P.; Weber, W. P. *J. Am. Chem. Soc.* **1980**, *102*, 6095–6097.

(4) Ragharachari, K.; Chandrasekhar, J.; Gordon, M. S.; Dykema, K. J. *J. Am. Chem. Soc.* **1984**, *106*, 5853–5859.

(5) Recently Ando et al. have reported the observation of a silacarbonyl ylide from the reaction of dimesitylsilylene with tetramethyl-2-indanone. Ando, W.; Hagiwara, K.; Sekiguchi, A. *Organometallics* **1987**, *6*, 2270–2271.

(6) Ishikawa, M.; Kumada, M. *J. Organomet. Chem.* **1972**, *42*, 325–332.

(7) Similar results are obtained by using diethyl ether as the Lewis base; the new band is also observed to have λ_{max} = 350 nm.

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