956 *Organometallics* 1986, *5*, 956-965

Synthesis, Structure, and Reactivity of the Formaldehyde Complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^2\text{-}H_2C{=}O)]^+PF_6^-$

William E. Buhro,[1] Savas Georgiou,[1a] Jesûs M. Fernández,[1a] Alan T. Patton,[1]
Charles E. Strouse,[1b] and J. A. Gladysz*[1,2]

Departments of Chemistry, University of Utah, Salt Lake City, Utah 84112, and University of California, Los Angeles, California 90024

Received November 12, 1985

Reaction of $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)({=}CH_2)]^+PF_6^-$ with $C_6H_5I^+\text{-}O^-$ gives formaldehyde complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^2\text{-}H_2C{=}O)]^+PF_6^-$ (**1**, 83%), which is characterized by X-ray crystallography. The $\eta^2\text{-}H_2C{=}O$ ligand adopts a conformation such that overlap of its π^* orbital with the rhenium fragment HOMO is maximized, and its oxygen terminus is syn to the PPh_3. Extended Hückel MO calculations on model compound $[(\eta^5\text{-}C_5H_5)Re(NO)(PH_3)(\eta^2\text{-}H_2C{=}O)]^+$ predict a similar conformational energy minimum. Complex **1** slowly reacts with CD_3CN (18 days, 25 °C) to give $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CD_3CN)]^+PF_6^-$ (**2**-d_3, 67–92%) and rapidly reacts with NaI (acetone, 25 °C) to precipitate $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^2\text{-}H_2C{=}O)]^+I^-$ (**3**, 68%). Addition of **3** to CH_3OH rapidly gives $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(I)$ (**4**, 65%). Unlike previously synthesized (neutral) $\eta^2\text{-}H_2C{=}O$ complexes, **1** undergoes nucleophilic additions but not well-defined electrophilic additions. Thus, addition of PR_3 to **1** gives $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(OCH_2PR_3)]^+PF_6^-$ (**5**, R = Ph, 89%; **6**, R = Me, 85%). Reaction of **1** with formyl complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CHO)$ gives methoxide complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(OCH_3)$ (**7**, 52%) and $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CO)]^+PF_6^-$. Attempted addition of $(\eta^5\text{-}C_5H_5)Co(CO)(PMe_3)$ to **1** in acetone-d_6 gives $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^1\text{-}(CD_3)_2C{=}O)]^+PF_6^-$ (**8**-d_6). The relationship of this chemistry to metal-catalyzed reactions involving formaldehyde is discussed.

Introduction

Formaldehyde is an exceedingly reactive organic molecule that is thermodynamically unstable with respect to trimerization and oligomerization.[3] It is of great importance in organic synthesis,[4] molecular photochemistry, and photophysics.[5] Since ligation to a transition metal often stabilizes reactive molecules, coordination complexes of formaldehyde should facilitate study of the $H_2C{=}O$ moiety.

Formaldehyde complexes are also involved in many important metal-catalyzed reactions. For example, a ruthenium–formaldehyde complex is believed to be a pivotal intermediate in the partitioning of CO/H_2 between methanol and glycol products over homogeneous ruthenium catalysts.[6,7] Formaldehyde can be hydroformylated over homogeneous rhodium catalysts to glycolaldehyde.[8] Methanol can be converted to formaldehyde and hydrogen over homogeneous ruthenium catalysts.[9] The study of isolable formaldehyde complexes can further understanding of the mechanisms of these catalytic reactions.

Surprisingly, isolable formaldehyde complexes were unknown prior to 1979, when Roper reported the synthesis of $Os(CO)_2(PPh_3)_2(\eta^2\text{-}H_2C{=}O)$.[10] Following this important discovery, formaldehyde complexes $Fe(CO)_2(P(OMe)_3)_2(\eta^2\text{-}H_2C{=}O)$,[11] $(\eta^5\text{-}C_5H_5)_2V(\eta^2\text{-}H_2C{=}O)$,[12] $(\eta^5\text{-}C_5H_5)_2Mo(\eta^2\text{-}H_2C{=}O)$,[13] $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^2\text{-}H_2C{=}O)]^+PF_6^-$ (**1**),[14] $(\eta^5\text{-}C_5H_5)Re(CO)_2(\eta^2\text{-}H_2C{=}O)$,[11c] and $W(H_2)(PMe_3)_4(\eta^2\text{-}H_2C{=}O)$[15] were isolated by Berke, Floriani, ourselves, M. L. H. Green, and Herberich. The synthesis of bridging $\eta^2\text{-}H_2C{=}O$ complexes,[16] and the spectroscopic observation of heterogeneous formaldehyde complexes[17] and unstable homogeneous formaldehyde complexes,[18] have also been described.[19] In this paper, we provide a full account of the synthesis, structure, and reactivity of the rhenium formaldehyde complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^2\text{-}H_2C{=}O)]^+PF_6^-$ (**1**). A portion of this study has been communicated.[14]

---

[1] (a) University of Utah. (b) University of California.

[2] To whom correspondence should be addressed at the University of Utah.

[3] Gerberich, H. R.; Stautzenberger, A. L.; Hopkins, W. C. In *Kirk-Othmer Encyclopedia of Chemical Technology*, 3rd ed.; Wiley-Interscience: New York, 1980; Vol. 11, pp 231-250.

[4] Fieser, M. *Reagents for Organic Synthesis*; Wiley-Interscience: New York, 1984; Vol. 11, pp 240-241 and references therein to previous volumes.

[5] See ref 3-23 of: Pope, S. A.; Hillier, I. H.; Guest, M. F. *J. Am. Chem. Soc.* **1985**, *107*, 3789.

[6] Dombek, B. D. *Adv. Catal.* **1983**, *32*, 325.

[7] See also: (a) Fahey, D. R. *J. Am. Chem. Soc.* **1981**, *103*, 136. (b) Rathke, J. W.; Feder H. M. In *Catalysis of Organic Reactions*; Moser, W. R., Ed.; Marcel Dekker: New York, 1981; p 209. (c) Hinderman, J.-P.; Schleiffer, E.; Idriss, H.; Kiennemann, A. *J. Mol. Catal.* **1985**, *33*, 133.

[8] Chan, A. S. C.; Carroll, W. E.; Willis, D. E. *J. Mol. Cat.* **1983**, *19*, 377.

[9] Shinoda, S.; Itagaki, H.; Saito, Y. *J. Chem. Soc., Chem. Commun.* **1985**, 860.

[10] (a) Brown, K. L.; Clark, G. R.; Headford, C. E. L.; Marsden, K.; Roper, W. R. *J. Am. Chem. Soc.* **1979**, *101*, 503. (b) Clark, G. R.; Headford, C. E. L.; Marsden, K.; Roper, W. R. *J. Organomet. Chem.* **1982**, *231*, 335. (c) Headford, C. E. L.; Roper, W. R. *Ibid.* **1983**, *244*, C53.

[11] (a) Berke, H.; Bankhardt, W.; Huttner, G.; von Seyerl, J.; Zsolnai, L. *Chem. Ber.* **1981**, *114*, 2754. (b) Berke, H.; Huttner, G.; Weiler, G.; Zsolnai, L. *J. Organomet. Chem.* **1981**, *219*, 353. (c) Berke, H.; Birk, R.; Huttner, G.; Zsolnai, L. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1984**, *39B*, 1380.

[12] Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Am. Chem. Soc.* **1982**, *104*, 2019.

[13] (a) Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Am. Chem. Soc.* **1985**, *107*, 2985. (b) Herberich, G. E.; Okuda, J. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 402.

[14] Buhro, W. E.; Patton, A. T.; Strouse, C. E.; Gladysz, J. A., McCormick, F. B.; Etter, M. C. *J. Am. Chem. Soc.* **1983**, *105*, 1056.

[15] (a) Green, M. L. H.; Parkin, G.; Moynihan, K. J.; Prout, K. *J. Chem. Soc., Chem. Commun.* **1984**, 1540. (b) Green, M. L.; Parkin, G. *Ibid.* **1986**, 90.

[16] (a) Threlkel, R. S.; Bercaw, J. E. *J. Am. Chem. Soc.* **1981**, *103*, 2650. (b) Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Ibid.* **1983**, *105*, 1690. (c) Kropp, K.; Skibbe, V.; Erker, C.; Krüger, C. *Ibid.* **1983**, *105*, 3353. (d) Barger, P. T.; Bercaw, J. E. *Organometallics* **1984**, *3*, 278.

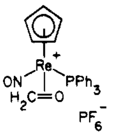
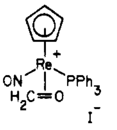
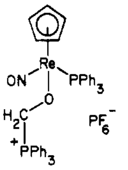
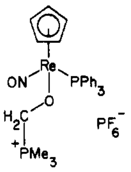
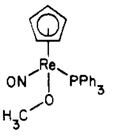
[17] (a) Wang, G.-W.; Hattori, H.; Itoh, H.; Tanabe, K. *J. Chem. Soc., Chem. Commun.* **1982**, 1256. (b) Anton, A. B.; Parmeter, J. E.; Weinberg, W. H. *J. Am. Chem. Soc.* **1985**, *107*, 5558.

[18] (a) $Pt(PPh_3)_2(\eta^2\text{-}H_2C{=}O)$: Head, R. A. *J. Chem. Soc., Dalton Trans.* **1982**, 1637. (b) See also: Chaudret, B. N.; Cole-Hamilton, D. J.; Nohr, R. S.; Wilkinson, G. *Ibid.* **1977**, 1546.

[19] Theoretical study of Li^+, $Na^+/H_2C{=}O$ complexes: Raber, D. J.; Raber, N. K.; Chandrasekhar, J.; Schleyer, P. V. R. *Inorg. Chem.* **1984**, *23*, 4076.

0276-7333/86/2305-0956$01.50/0

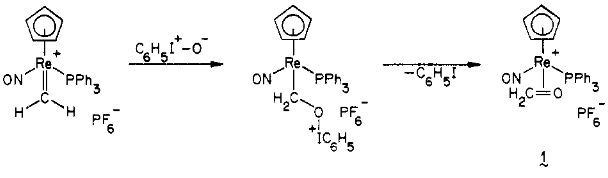
Table I. IR and NMR Characterization of New Rhenium Complexes

complex	IR, cm^{-1} (KBr)	^{1}H NMR,[a] δ	^{31}P{^{1}H} NMR,[b] ppm	^{13}C{^{1}H} NMR,[c] ppm
 1	3120 w, 3062 w, 2969 w, 2926 w, 2878 w, $\nu_{N{\equiv}O}$ 1737 vs, 1587 w, 1575 w, 1484 m, 1438 s, 1420 m, 1360 w, 1315 w, 1208 m, 1163 w, 1098 s, 1074 w, 1056 m, 1027 w, 1019 w, 999 w, $\nu_{P{-}F}$ 842 vs vbr, 749 m, 711 m, 694 s	7.76–7.53 (m, 15 H), 6.40 (d, J_{HP} = 0.6 Hz, 5 H), 4.93 (dd, J_{HH} = 16.8 Hz, J_{HP} = 2.3 Hz, 1 H), 4.39 (dd, J_{HH} = 16.8 Hz, J_{HP} = 1.3 Hz, 1 H)[d,e]	10.31 (s)[d]	PPh$_3$ at 134.51 (d, J_{CP} = 10.8 Hz, o), 133.70 (s, p), 130.61 (d, J_{CP} = 11.3 Hz, m), 128.36 (d, J_{CP} = 59.7 Hz, i); 100.40 (s, C$_5$H$_5$), 60.56 (s, CH$_2$)[d,f]
 3	3088 m, 3053 m, 3021 w, 3006 w, 2989 w, 2012 w, 1988 w, $\nu_{N{\equiv}O}$ 1732 vs, 1710 s, 1587 w, 1572 w, 1480 m, 1434 s, 1423 m, 1410 m, 1356 w, 1311 w, 1206 w, 1190 m, 1158 w, 1111 w, 1097 s, 1073 w, 1063 w, 1053 w, 1045 w, 1026 w, 1009 w, 996 w, 967 w, 890 w, 869 m, 849 w, 749 m, 710 m, 694 s	7.71–7.60 (m, 9 H), 7.45–7.36 (m, 6 H), 6.36 (s, 5 H), 4.82 (d, J_{HH} = 16.6 Hz, 1H), 4.30 (d, J_{HH} = 16.6 Hz, 1H)[g]		
 5	3222–3063 w, 2792 w, $\nu_{N{\equiv}O}$ 1630 vs, 1588 w, 1575 w, 1482 m, 1438 s, 1422 m, 1338 w, 1316 w, 1275 w, 1186 w, 1163 w, 1117 m, 1095 m, 1058 m, 1027 w, 1017 w, 998 m, 908 w, $\nu_{P{-}F}$ 837 vs vbr, 760 m, 745 m, 721 m, 699 m, 689 s, 617 w	7.89–7.26 (m, 30 H), 5.89 (d, J_{HH} = 13.7 Hz, 1 H), 5.60 (dd, J_{HH} = 13.7 Hz, J_{HP} = 0.8 Hz, 1 H), 5.44 (s, 5 H)[d,h]	16.73 (s), 14.13 (s)[d,i]	CH$_2$PPh$_3$ at 135.81 (d, J_{CP} = 2.7 Hz, p), 135.23 (d, J_{CP} = 9.8 Hz, o), 131.21 (d, J_{CP} = 12.5 Hz, m), 119.98 (d, J_{CP} = 81.5 Hz, i); 83.53 (dd, $^1J_{CP}$ = 52.2 Hz, $^3J_{CP}$ = 7.3 Hz, CH$_2$); RePPh$_3$ at 135.56 (d),[j] 135.00 (d, J_{CP} = 11.0 Hz, o), 131.88 (d, J_{CP} = 1.7 Hz, p), 129.84 (d, J_{CP} = 10.1 Hz, m); 92.43 (s, C$_5$H$_5$)[d,h]
 6	3244 w, 3116 w, 3055 w, 3005 w, 2925 w, 2865 w, 2790 w, $\nu_{N{\equiv}O}$ 1634 vs, 1587 w, 1573 w, 1482 m, 1436 m, 1322 w, 1301 m, 1269 w, 1186 w, 1159 w, 1096 m, 1063 m, 1027 w, 982 m, 878 m, $\nu_{P{-}F}$ 843 vs vbr, 775 w, 751 m, 736 m, 705 m, 695 s, 649 m, 619 w	7.56–7.45 (m, 15 H), 5.48 (s, 5 H), 4.62 (dd, J_{HH} = 13.3 Hz, J_{HP} = 1.4 Hz, 1 H), 4.52 (dd, J_{HH} = 13.2 Hz, J_{HP} = 0.7 Hz, 1 H), 1.53 (d, J_{HP} = 14.5 Hz, 9 H)[d,k]	22.14 (s), 18.61 (s)[d,l]	PPh$_3$ at 135.73 (d),[j] 135.08 (d, J_{CP} = 10.9 Hz, o), 131.97 (s, p), 129.93 (d, J_{CP} = 10.1 Hz, m); 92.40 (s, C$_5$H$_5$), 80.80 (dd, $^1J_{CP}$ = 60.1 Hz, $^3J_{CP}$ = 6.9 Hz, CH$_2$), 5.26 (d, J_{CP} = 52.9 Hz, PMe$_3$)[d,k]
 7	3233 w, 3069 w, 3055 w, 2886 w, 2864 w, 2838 w, 2820 w, 2763 s, $\nu_{N{\equiv}O}$ 1633 vs, 1585 m, 1569 m, 1482 m, 1436 s, 1427 m, 1415 w, 1309 w, 1185 w, 1163 w, 1095 s, 1061 s, 1049 s, 1028 w, 1000 m, 901 w, 852 w, 831 m, 812 w, 792 w, 750 s, 696 s, 620 w	7.49–7.35 (m, 15 H), 5.25 (s, 5 H), 3.95 (s, 3 H)[m]	16.09 (s)[m]	PPh$_3$ at 134.49 (d, J_{CP} = 50.3 Hz, i), 134.07 (d, J_{CP} = 10.9 Hz, o), 130.66 (s, p), 128.72 (d, J_{CP} = 10.8 Hz, m); 91.29 (s, C$_5$H$_5$), 75.67 (d, J_{CP} = 5.4 Hz, CH$_3$)[n]

[a] At 200 or 300 MHz and ambient probe temperature and referenced to internal Si(CH$_3$)$_4$. [b] At 32 MHz and ambient probe temperature and referenced to external 85% H$_3$PO$_4$, except where noted; PF$_6^-$ resonances are not reported. [c] At 50 or 75 MHz and ambient probe temperature and referenced to internal Si(CH$_3$)$_4$. Assignments of resonances to the PPh$_3$ carbons were made as follows. Both ipso (i) and para (p) carbon resonances were easily distinguished on the basis of intensity and J_{PC}. The meta (m) resonance was assigned according to the proposal of Mann that it is the one closest to the chemical shift of benzene: Mann, B. E. *J. Chem. Soc., Perkin Trans. 2* **1972**, 30. ^{13}C NMR assignments in a number of phenylphosphonium salts and phenylphosphine complexes have been made in a manner consistent with this proposal: Ganson, O. A.; Kimura, B. Y. *J. Chem. Soc., Chem. Commun.* **1970**, 1621. Verstuyft, A. W.; Redfield, D. A.; Cary, L. W.; Nelson, J. H. *Inorg. Chem.* **1976**, *15*, 1128. Weigert, F. J.; Roberts, J. D. *Ibid.* **1973**, *12*, 313. Gray, G. A. *J. Am. Chem. Soc.* **1973**, *95*, 7736. Albright, T. A.; Freeman, W. J.; Schweizer, E. E. *Ibid.* **1975**, *97*, 2942, 2947. [d] In acetone-d$_6$. [e] Data in CD$_2$Cl$_2$: δ 5.99 (s, 5 H), 4.75 (dd, J_{HH} = 16.7 Hz, J_{HP} = 2.2 Hz, 1 H), 4.30 (dd, J_{HH} = 16.7 Hz, J_{HP} = 1.1 Hz, 1 H). [f] Coupled spectrum (obtained with decoupler gated on during pulse delay and off during acquisition) shows J_{CH} of 179 and 184 Hz for CH$_2$ resonance. [g] In Me$_2$SO-d_6 at 32 °C; sample stored at −78 °C prior to analysis. [h] Resonances for 1 also detectable; see text. [i] At −19 °C. [j] Downfield line of ipso carbon doublet; upfield line obscured. [k] CH$_2$Cl$_2$ solvate also present. [l] At −30 °C. [m] In CD$_2$Cl$_2$. [n] In CDCl$_3$.

Results

Synthesis of [(η^5-C_5H_5)Re(NO)(PPh_3)(η^2-$H_2C{=}O$)]$^+PF_6^-$ (1). In previous work, we have shown that the electrophilic methylidene complex [(η^5-C$_5$H$_5$)Re(NO)(PPh$_3$)(=CH$_2$)]$^+$PF$_6^-$ is readily attacked by neutral and anionic heteronucleophiles (:Nu) to give adducts with a ReCH$_2$Nu linkage.[20] Hence, we thought that a nucleophilic oxidizing agent X$^+$–O$^-$ might react to give an adduct that would yield 1 upon departure of leaving group X. Addition of anhydrous (CH$_3$)$_3$N$^+$–O$^-$ to [(η^5-C$_5$H$_5$)Re(NO)(PPh$_3$)(=CH$_2$)]$^+$PF$_6^-$ (CH$_2$Cl$_2$; −78 °C, then warming) gave, as assayed by ^{1}H NMR, several products, one of which was 1. However, iodosobenzene, C$_6$H$_5$I$^+$–O$^-$, which is insoluble in CH$_2$Cl$_2$, and [(η^5-C$_5$H$_5$)Re(NO)(PPh$_3$)(=CH$_2$)]$^+$PF$_6^-$ reacted to give 1 in 83% yield after workup. This transformation can be visualized as proceeding via the intermediate shown in eq 1.



1

(1)

Complex 1 was characterized as summarized in Table I. Features of a cationic [(η^5-C$_5$H$_5$)Re(NO)(PPh$_3$)(L)]$^+$ complex were readily apparent (IR $\nu_{N{\equiv}O}$; ^{1}H and ^{13}C NMR η^5-C$_5$H$_5$ chemical shifts). The ^{1}H NMR spectrum, illus-

---

(20) Tam, W.; Lin, G.-Y.; Wong, W.-K.; Kiel, W. A.; Wong, V. K.; Gladysz, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 141.

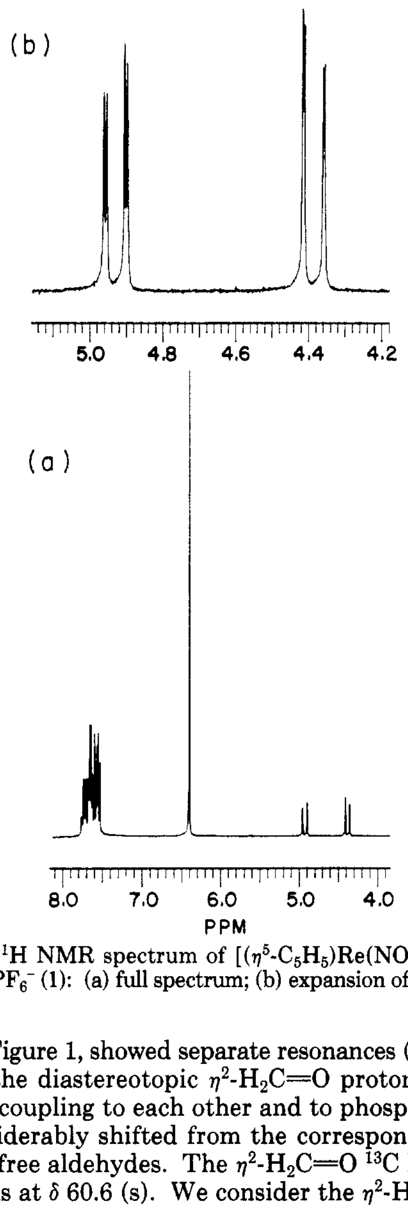


Figure 1. ^1H NMR spectrum of $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^2\text{-}H_2C{=}O)]^+PF_6^-$ (1): (a) full spectrum; (b) expansion of $\eta^2\text{-}H_2C{=}O$ resonances.

trated in Figure 1, showed separate resonances (δ 4.93 and 4.38) for the diastereotopic $\eta^2\text{-}H_2C{=}O$ protons. These exhibited coupling to each other and to phosphorus and were considerably shifted from the corresponding resonances of free aldehydes. The $\eta^2\text{-}H_2C{=}O$ ^{13}C NMR resonance was at δ 60.6 (s). We consider the $\eta^2\text{-}H_2C{=}O$ ^1H and ^{13}C NMR chemical shifts, and the absence of an IR $\nu_{C=O}$, to be the most diagnostic spectroscopic evidence for a η^2-coordination mode. Metal η^1-aldehyde complexes such as $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(\eta^1\text{-}(i\text{-}C_3H_7)HC{=}O)]^+PF_6^-$ show downfield aldehydic ^1H NMR resonances (δ 9.58) and slightly shifted IR $\nu_{C=O}$ (1660 cm^{-1}).[21,22]

The $\eta^2\text{-}H_2C{=}O$ ^1H NMR resonances in Figure 1 did not coalesce at temperatures as high as 100 °C ($CDCl_2CDCl_2$, 200 MHz). From this observation, $\Delta G^{\ddagger}_{373}$ for any process capable of interconverting the two $\eta^2\text{-}H_2C{=}O$ protons must be greater than 17.5 kcal/mol.[23]

The dideuterated complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^2\text{-}D_2C{=}O)]^+PF_6^-$ (1-d_2) was similarly prepared from[24] $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)({=}CD_2)]^+PF_6^-$ and $C_6H_5I^+\text{-}O^-$. The IR spectrum of 1-d_2 showed new absorbances at 2280 and 2130 cm^{-1} and was lacking the 2878 cm^{-1} absorbance of 1. The latter two differ by a factor of 1.35, which is close to the 1.41 expected theoretically for corresponding $\nu_{C\text{-}D}$ and $\nu_{C\text{-}H}$.[25] The analogous absorptions for $\eta^2\text{-}H_2C{=}O$ (2940 cm^{-1}) and $\eta^2\text{-}D_2C{=}O$ (2225 cm^{-1}) on Ru(001) differ by a factor of 1.32.[17b]

Table II. Summary of Crystallographic Data for $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^2\text{-}H_2C{=}O)]^+PF_6^-$ (1)

mol formula	$C_{24}H_{22}F_6NO_2P_2Re$
mol wt	718.6
cryst system	monoclinic
space group	$P2_1$
cell dimens (−158 °C)	
a, Å	10.113 (3)
b, Å	18.928 (7)
c, Å	13.300 (4)
β, deg	105.03 (2)
V, Å^3	2458 (1)
Z	4
d_{obsd}, g/cm^3 (25 °C)	1.84
d_{calcd}, g/cm^3 (−158 °C)	1.91
cryst dimens, mm	0.11 × 0.10 × 0.20
radiatn, Å	λ(Mo Kα), 0.71069
data collectn method	θ–2θ
scan speed, deg/min	8.0
reflctns measured	$+h,+k,\pm l$
scan range	Kα_1 − 1.0 to Kα_2 + 1.0
total bkgd time/scan time	0.0
no. of reflctns between std	97
total unique data	4847
obsd data, $I > 3\sigma(I)$	4090
abs coeff (μ), cm^{-1}	51.21
min absorptn correctn	0.7538
max absorptn correctn	0.8125
av absorptn correctn	0.7863
no. of variables	387
$R = \sum\|\|F_o\| - \|F_c\|\|/\sum\|F_o\|$	0.043
$R_w = [\sum w(\|F_o\| - \|F_c\|)^2/\sum w(F_o)^2]^{1/2}$	0.052
goodness of fit	1.49

Structure of 1. The structure of 1 was further investigated by X-ray crystallography. Suitable single crystals were obtained from CH_2Cl_2/hexanes, and X-ray data were obtained under the conditions summarized in Table II. The unit cell was found to be monoclinic, with the lattice parameters listed in Table II. Refinement, described in the Experimental Section, was complicated by NO/$\eta^2\text{-}H_2C{=}O$ disorder for *one* of the two non-symmetry-related $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^2\text{-}H_2C{=}O)]^+$ cations in the unit cell. The data that follow are for the nondisordered cation. The $\eta^2\text{-}H_2C{=}O$ hydrogen atoms could not be located.

The structure of the cation of 1 is shown stereoscopically in Figure 2. Other views of the $\eta^2\text{-}H_2C{=}O$ ligand are given in Figure 3. Important bond distances and angles are compiled in Table III, and positional parameters are given in Table IV. Since thermal parameters, structure factors, and packing diagrams were included in the supplementary material of our communication,[14] and elsewhere,[26] they are not republished here.

As can be seen in Figure 3a, the $\eta^2\text{-}H_2C{=}O$ ligand is oriented with the oxygen syn to the PPh_3 ligand. The angle of the $\overline{Re{-}C{=}O}$ plane with the Re-P vector is 15°. Figure 3b shows that the $\eta^2\text{-}H_2C{=}O$ ligand is "slipped". Consider point X, where the C–O bond intersects the vector drawn from the rhenium perpendicular to the C–O bond. Point X is considerably closer to oxygen (0.578 Å) than to carbon (0.797 Å).

Extended Hückel MO calculations were conducted on the model compound $[(\eta^5\text{-}C_5H_5)Re(NO)(PH_3)(\eta^2\text{-}H_2C{=}O)]^+$ as described in the Experimental Section. Figure 4 shows the variation in E_{total} and the HOMO and LUMO

---

(21) Foxman, B. M.; Klemarczyk, P. T.; Liptrot, R. E.; Rosenblum, M. *J. Organomet. Chem.* **1980**, *187*, 253.

(22) A variety of related η^1 and η^2 ketone and aldehyde complexes will be described shortly: Fernández, J. M., unpublished results, University of Utah.

(23) Sandström, J. *Dynamic NMR Spectroscopy*; Academic Press: New York, 1982.

(24) Merrifield, J. H.; Lin, G.-Y.; Kiel, W. A.; Gladysz, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 5811.

(25) Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectrometric Identification of Organic Compounds*, 4th ed.; Wiley: New York, 1981; p 97.

(26) Buhro, W. E. Ph.D. Thesis, UCLA, 1985.

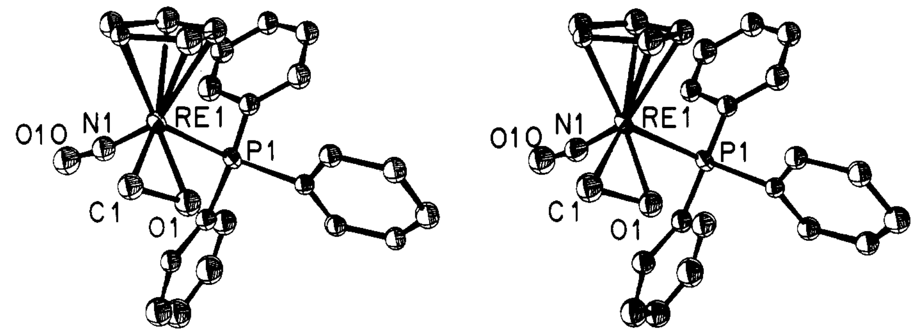


Figure 2. Stereoview of the cation of $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^2\text{-}H_2C{=}O)]^+PF_6^-$ (1).

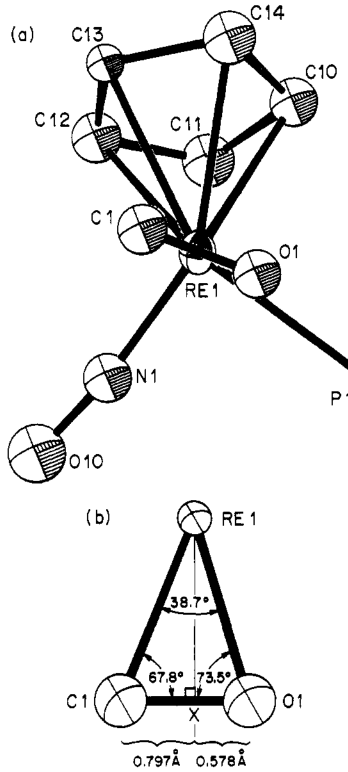
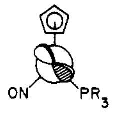


Figure 3. Additional views of the η^2-$H_2C{=}O$ ligand in $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^2\text{-}H_2C{=}O)]^+PF_6^-$ (1): (a) Newman projection; (b) plane containing Re(1), C(1), and O(1).

energies as the η^2-$H_2C{=}O$ ligand is rotated. The absolute energy minimum at $\theta = 60°$ corresponds to an angle of the $\overline{\mathrm{Re{-}C{=}O}}$ plane with the Re-P vector of 30°.

At the energy maximum at $\theta = 180°$, the HOMO was found to be the rhenium centered orbital Ia and the



I
a, R = H
b, R = Ph

LUMO was composed largely of $H_2C{=}O$ π^* and $N{\equiv}O$ π^* contributions. Rotation of η^2-$H_2C{=}O$ in either direction markedly altered the character of these orbitals. In addition, the HOMO was stabilized and the LUMO concurrently destabilized. Thus, the HOMO energy and E_{total} are in phase, while the LUMO energy is nearly perfectly out of phase with both. The θ dependence of the HOMO energy accounts for nearly 70% of the θ dependence of E_{total}.

Chemistry of 1. We sought to address several fundamental questions concerning the reactivity of 1. Would the η^2-$H_2C{=}O$ ligand be readily displaced? Would the η^2-$H_2C{=}O$ ligand be activated towards attack? Hence, we investigated reactions of 1 with nucleophiles and electrophiles.

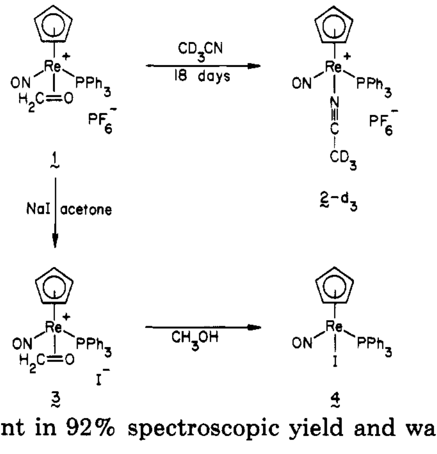
Table III. Selected Bond Distances and Angles in 1[a]

from	to	dist, Å
C(1)	O(1)	1.374 (19)
C(1)	Re(1)	2.108 (18)
O(1)	Re(1)	2.036 (11)
N(1)	Re(1)	1.735 (14)
P(1)	Re(1)	2.455 (4)
N(1)	O(10)	1.184 (17)
C(10)	C(11)	1.424 (24)
C(10)	C(14)	1.458 (24)
C(10)	Re(1)	2.305 (17)
C(11)	C(12)	1.378 (25)
C(11)	Re(1)	2.283 (18)
C(12)	C(13)	1.397 (23)
C(12)	Re(1)	2.265 (17)
C(13)	C(14)	1.430 (23)
C(13)	Re(1)	2.344 (14)
C(14)	Re(1)	2.383 (18)

from	thru	to	angle, deg
O(1)	C(1)	Re(1)	67.81 (85)
C(1)	O(1)	Re(1)	73.51 (86)
P(1)	Re(1)	N(1)	88.35 (48)
P(1)	Re(1)	O(1)	79.07 (32)
P(1)	Re(1)	C(1)	116.29 (50)
N(1)	Re(1)	O(1)	105.66 (54)
N(1)	Re(1)	C(1)	95.85 (66)
O(1)	Re(1)	C(1)	38.67 (53)
Re(1)	N(1)	O(10)	171.74 (13)
C(11)	C(10)	C(14)	108.50 (149)
C(12)	C(11)	C(10)	107.01 (159)
C(11)	C(12)	C(13)	110.92 (154)
C(12)	C(13)	C(14)	108.29 (141)
C(13)	C(14)	C(10)	105.24 (147)

[a] See Figure 3 for atomic numbering.

Complex 1 slowly converted to acetonitrile complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(NCCD_3)]^+PF_6^-$ (2-d_3)[24] in CD_3CN (0.18 M) at room temperature (eq 2). After 18 days, 2-d_3 was present in 92% spectroscopic yield and was subse-



(2)

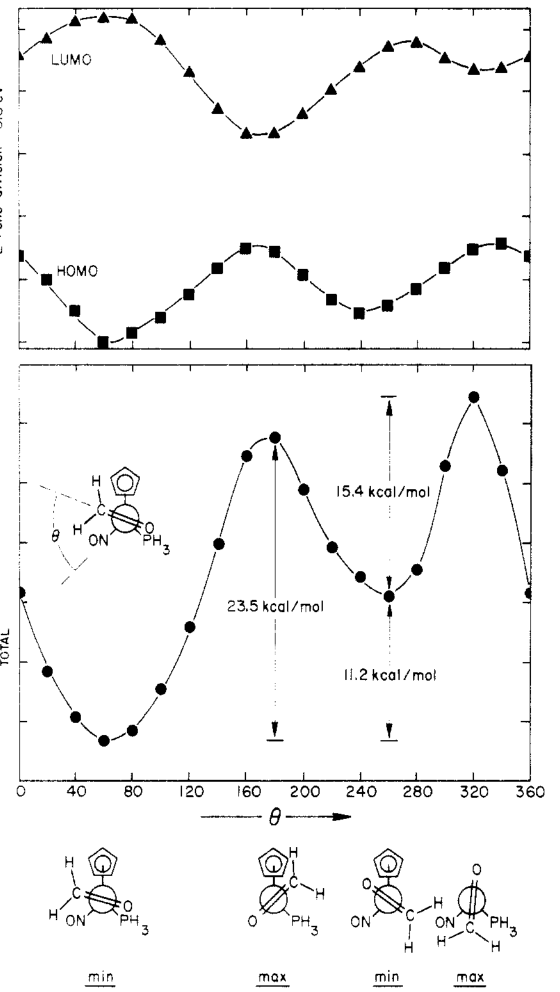


Figure 4. Variation in E_{total} and HOMO and LUMO energies as the η^2-$H_2C{=}O$ ligand is rotated in $[(\eta^5\text{-}C_5H_5)Re(NO)(PH_3)(\eta^2\text{-}H_2C{=}O)]^+$ (calculated by the extended Hückel method with weighted H_{ij} formula).

quently isolated in 67% yield. In a separate experiment, conversion of 1 (0.056 M) to 2-d_3 was 48% complete after 19 h at 51 °C, and 82% complete after 41.3 h. Treatment of 1 with CO (25 °C, CH_2Cl_2, 225 psi, 30 h) gave ca. 25% conversion to $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CO)]^+PF_6^-$,[20] as assayed by IR. Treatment of 1 with $H_2C{=}CH_2$ (25 °C, CH_2Cl_2, 200 psi, 36 h) did not give any ethylene complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H_2C{=}CH_2)]^+PF_6^-$,[24] as assayed by IR and ^1H NMR.

Reaction of 1 with NaI (25 °C, acetone) gave a precipitate that was either sparingly soluble or unstable in common organic solvents. Spectroscopic (Table I) and elemental analyses showed this material to be $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^2\text{-}H_2C{=}O)]^+I^-$ (**3**, 68%; eq 2). When **3** was added to CH_3OH, an orange solution formed and then purple iodide complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(I)$ (**4**, 65%)[27] rapidly precipitated.

Reaction of 1 with PPh_3 (25 °C, CH_2Cl_2) was expected to give the known substitution product $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)_2]^+PF_6^-$.[20,24] Instead, a new compound crystallized that was formulated as the addition product $[(\eta^5\text{-}C_5H_5)Re(NO)(OCH_2PPh_3)]^+PF_6^-$ (**5**; eq 3). This structural assigment, which corresponds to phosphorus addition to carbon (ReOCP), was favored over the regioisomer derivable from phosphorus addition to oxygen (ReCOP) on the basis of NMR data (Table I). Specifically,

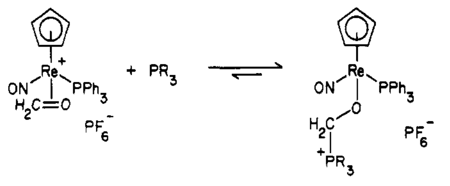
Table IV. Positional Parameters for Non-Hydrogen Atoms in 1[a]

atom	*x*	*y*	*z*
Re(1)	0.26957 (6)	0.0000	0.04292 (4)
Re(2)	0.71406 (6)	0.27469 (5)	0.39145 (5)
P(1)	0.3433 (4)	0.0489 (2)	-0.1047 (3)
P(2)	0.6191 (4)	0.2357 (2)	0.5304 (3)
P(10)	0.8835 (4)	0.0012 (3)	0.2440 (3)
P(20)	0.0820 (5)	0.2675 (3)	0.1630 (4)
F(11)	0.7940 (11)	0.0544 (6)	0.1572 (9)
F(12)	0.7963 (11)	0.0185 (7)	0.3235 (9)
F(13)	0.9874 (11)	0.0616 (7)	0.2911 (9)
F(14)	0.7761 (11)	-0.0608 (6)	0.1958 (8)
F(15)	0.9715 (13)	-0.0541 (7)	0.3287 (9)
F(16)	0.9705 (10)	-0.0192 (5)	0.1625 (8)
F(21)	0.0294 (12)	0.3291 (7)	0.2236 (9)
F(22)	0.2349 (11)	0.2868 (9)	0.2228 (9)
F(23)	-0.0735 (11)	0.2488 (6)	0.1023 (8)
F(24)	0.0901 (10)	0.3214 (6)	0.0715 (7)
F(25)	0.0762 (14)	0.2131 (8)	0.2528 (12)
F(26)	0.1334 (14)	0.2064 (7)	0.1010 (10)
C(1)	0.2257 (18)	-0.1090 (9)	0.0369 (13)
N(1)	0.1042 (14)	0.0269 (7)	-0.0181 (10)
O(1)	0.3006 (11)	-0.0901 (6)	-0.0315 (8)
O(10)	-0.0099 (13)	0.0475 (7)	-0.0475 (9)
C(10)	0.4643 (17)	0.0475 (9)	0.1522 (13)
C(11)	0.3510 (19)	0.0923 (10)	0.1519 (14)
C(12)	0.2621 (18)	0.0539 (10)	0.1934 (13)
C(13)	0.3148 (15)	-0.0133 (7)	0.2239 (11)
C(14)	0.4439 (20)	-0.0197 (9)	0.1995 (14)
O(2)	0.6678 (20)	0.3715 (11)	0.4660 (15)
C(2)	0.7625 (33)	0.3946 (18)	0.4131 (24)
O(2′)	0.8733 (28)	0.2183 (16)	0.4880 (21)
N(2)	0.8763 (26)	0.2573 (13)	0.4660 (19)
N(2′)	0.7367 (36)	0.3597 (19)	0.4321 (27)
C(2′)	0.9337 (42)	0.2579 (20)	0.4222 (31)
O(20)	0.9868 (24)	0.2384 (12)	0.5091 (17)
O(20′)	0.7309 (31)	0.4203 (17)	0.4574 (24)
C(20)	0.6411 (18)	0.1845 (9)	0.2779 (13)
C(21)	0.7349 (21)	0.2272 (12)	0.2404 (16)
C(22)	0.6874 (22)	0.2913 (12)	0.2240 (16)
C(23)	0.5486 (19)	0.2963 (10)	0.2374 (14)
C(24)	0.5260 (16)	0.2296 (9)	0.2723 (12)
C(131)	0.2051 (16)	0.0473 (9)	-0.2252 (12)
C(132)	0.2024 (19)	0.0982 (10)	-0.2981 (14)
C(133)	0.1016 (22)	0.0914 (12)	-0.3992 (16)
C(134)	0.0140 (21)	0.0338 (11)	-0.4193 (16)
C(135)	0.0235 (22)	-0.0161 (11)	-0.3413 (16)
C(136)	0.1176 (17)	-0.0099 (9)	-0.2404 (13)
C(122)	0.5048 (15)	0.0066 (10)	-0.2349 (11)
C(123)	0.6259 (17)	-0.0213 (8)	-0.2491 (13)
C(124)	0.7268 (18)	-0.0499 (9)	-0.1763 (13)
C(125)	0.7110 (17)	-0.0540 (9)	-0.0703 (13)
C(126)	0.5903 (17)	-0.0263 (8)	-0.0511 (12)
C(121)	0.4893 (13)	0.0026 (9)	-0.1337 (10)
C(142)	0.5289 (18)	0.1594 (9)	-0.0611 (13)
C(143)	0.5692 (18)	0.2317 (10)	-0.0360 (14)
C(144)	0.4680 (16)	0.2806 (11)	-0.0393 (12)
C(145)	0.3332 (19)	0.2595 (10)	-0.0620 (14)
C(146)	0.2943 (18)	0.1923 (10)	-0.0821 (14)
C(141)	0.3942 (16)	0.1415 (8)	-0.0849 (12)
C(222)	0.4235 (15)	0.1261 (8)	0.4951 (11)
C(223)	0.3857 (18)	0.0561 (10)	0.4749 (13)
C(224)	0.4769 (15)	0.0064 (10)	0.4643 (11)
C(225)	0.6145 (18)	0.0237 (9)	0.4742 (13)
C(226)	0.6566 (18)	0.0955 (9)	0.5001 (13)
C(221)	0.5596 (15)	0.1455 (8)	0.5083 (12)
C(232)	0.4482 (18)	0.2899 (10)	0.6478 (13)
C(233)	0.3306 (20)	0.3208 (11)	0.6562 (15)
C(234)	0.2371 (22)	0.3482 (11)	0.5780 (16)
C(235)	0.2561 (21)	0.3445 (11)	0.4783 (16)
C(236)	0.3810 (20)	0.3127 (10)	0.4670 (14)
C(231)	0.4740 (17)	0.2841 (10)	0.5469 (12)
C(241)	0.7423 (16)	0.2363 (9)	0.6549 (12)
C(242)	0.8321 (20)	0.2995 (10)	0.6857 (14)
C(243)	0.9217 (23)	0.2980 (12)	0.7800 (18)
C(244)	0.9287 (21)	0.2445 (11)	0.8513 (15)
C(245)	0.8422 (20)	0.1884 (10)	0.8268 (14)
C(246)	0.7504 (19)	0.1820 (10)	0.7278 (14)

[a] The primed atoms are from disordered ligands.

---

[27] Merrifield, J. H.; Fernández, J. M.; Buhro, W. E.; Gladysz, J. A. *Inorg. Chem.* **1984**, *23*, 4022.



(3)

1

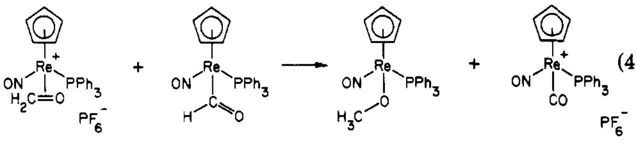
5, R = C_6H_5
6, R = CH_3

the CH_2 carbon of 5 exhibited a ^{13}C NMR J_{CP} (52 Hz) characteristic of carbon directly bound to phosphonium phosphorus.[28] Each of the diastereotopic CH_2 protons showed a characteristically small phosphonium salt $^2J_{PH}$ (<1 Hz),[29] and no other phosphorus couplings. Rhenium alkyl and ylide complexes of the formula $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2X)$, which are approximate models for the ReCOP regioisomer, show small $^2J_{PReC_\alpha}$ ($J \le 6$ Hz) and $^3J_{PReCH_\alpha}$ of 2–10 Hz.[20] Furthermore, $^2J_{POC_\alpha}$ and $^3J_{POCH_\alpha}$, couplings that would be present in the ReCOP regioisomer, are typically <12 Hz[30] and (depending upon dihedral angle) 5–10 Hz,[31] respectively.

When crystalline 5 was dissolved in acetone-d_6 (0.050 M), ^1H NMR analysis indicated a 84:16 ratio of 5 to formaldehyde complex 1. Analysis of the IR $\nu_{N\equiv O}$ (CH_2Cl_2) indicated an 87:13 ratio. When 5 was dissolved in CD_2Cl_2 at −73 °C, only 5 could be detected by ^1H NMR. The probe temperature was raised to −33 °C. Complexes 5 and 1 were then present in a 98:2 ratio. This ratio decreased upon warming and was not affected by subsequent cooling to −73 °C. We conclude from these observations that 1 and PPh_3 are in equilibrium with 5, $1 + PPh_3 \rightleftharpoons 5$, with a K_{eq} of ca. 9×10^2 M^{-1} (acetone, 25 °C).

In order to further our understanding of the PPh_3 addition reaction, we treated 1 with the more basic phosphine PMe_3. Crystalline adduct $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(OCH_2PMe_3)]^+PF_6^-{\cdot}CH_2Cl_2$ ($6{\cdot}CH_2Cl_2$) was subsequently isolated in 85% yield. This complex was not in equilibrium with any detectable amount of 1 in solution.

Addition of hydride to 1 was attempted next. When 1 was treated with $Li(C_2H_5)_3BH$ in CH_2Cl_2/THF or $NaBH_3CN$ in CH_3OH, spectroscopic evidence for the generation of methoxide complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(OCH_3)$ (7) was noted. However, numerous other products also formed. When 1 was treated with formyl complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CHO)$[20]—a good hydride donor—methoxide complex 7 and cation $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CO)]^+PF_6^-$ were subsequently isolated in 52% and 91% yields, respectively (eq 4). In an analogous ^1H NMR monitored experiment, these products formed in 74% and 99% yields vs. an internal standard. Complex 7 was also prepared in 93% yield from reaction of tosylate complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(OSO_2\text{-}p\text{-}C_6H_4CH_3)$[27] with $NaOCH_3$.



(4)

1 7

Methoxide complex 7 was very air sensitive in solution and was of limited stability in chlorinated solvents. It was spectroscopically characterized as summarized in Table I. The IR spectrum (Figure 5) showed several absorbances at 2890–2763 cm^{-1} not found in other $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(X)$ complexes, including a very sharp band at 2763 cm^{-1}. When 7 was treated with $Ph_3C^+PF_6^-$ in CH_2Cl_2, formaldehyde complex 1 and Ph_3COCH_3 formed in 15–20% and 42% yields, respectively, as assayed by ^1H NMR.

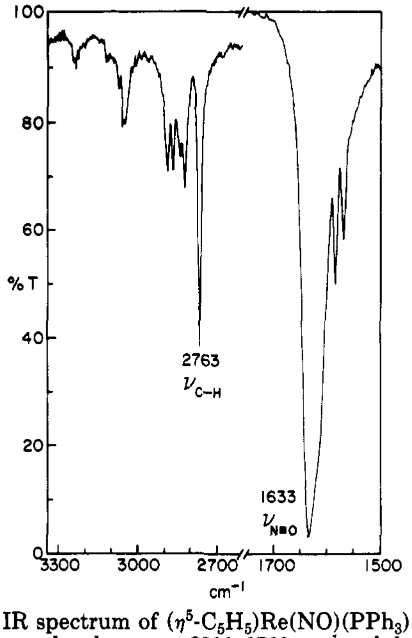
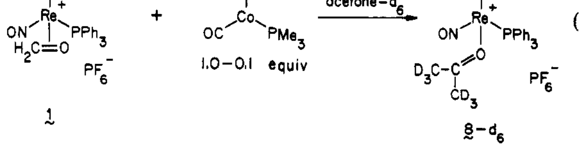


Figure 5. IR spectrum of $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(OCH_3)$ (7) showing unique absorbances at 2890–2763 cm^{-1} and their intensity relationship to $\nu_{N\equiv O}$ at 1633 cm^{-1}.

Addition of transition-metal nucleophiles to 1 was attempted. Reaction of 1 with $(\eta^5\text{-}C_5H_5)Co(CO)(PMe_3)$[32]—a very basic complex[33]—in acetone-d_6 was monitored by ^1H NMR. Over the course of 16 h, most of 1 was converted to a new product, 8-d_6 (δ 5.81; 58%), while most of the cobalt complex remained (69%). A similar experiment was conducted with 0.1 equiv of $(\eta^5\text{-}C_5H_5)Co(CO)(PMe_3)$. After 2 days, 8-$d_6$ and 1 were present in 49% and 22% yields, respectively. An identical experiment was conducted without cobalt complex. After 2 days, 8-d_6 and 1 were present in 15% and 74% yields. Complex 8-d_6 exhibited IR $\nu_{N\equiv O}$ and $\nu_{C=O}$ (cm^{-1}, thin film) of 1686 s and 1617 m and a $^{31}P\{^1H\}$ resonance (ppm, acetone-d_6, −30 °C) at 17.35 (s). On the basis of an independent synthesis, isolation, and complete structural characterization to be described elsewhere,[22] 8-d_6 was assigned the structure $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^1\text{-}(CD_3)_2C{=}O)]^+PF_6^-$ (eq 5).



(5)

1 8-d_6

Complex 5, shown above to be in equilibrium with 1 and PPh_3, was also treated with $(\eta^5\text{-}C_5H_5)Co(CO)(PMe_3)$ (acetone-d_6, 25 °C, 16 h). It was hoped that the μ,η^2-formaldehyde complex sought from eq 5, $(\eta^5\text{-}C_5H_5)$-

---

[28] Corresponding $^1J_{PC}$ in $[Ph_3PCH_2OCH_3]^+$, 69 Hz: Gray, G. A. *J. Am. Chem. Soc.* **1973**, *95*, 7736.

[29] Literature values for $^2J_{PH}$ in phosphonium salts $[Ph_3PCH_2OH]^+$, $[Ph_3PCH_2OCOCH_3]^+$, and $[Ph_3PCH_2OCH_3]^+$ are in the range 0–4 Hz: (a) Hendrickson, J. B.; Maddox, M. L.; Simms, J. J.; Kaesz, H. D. *Tetrahedron* **1964**, *20*, 449. (b) Gallagher, M. J. *Aust. J. Chem.* **1968**, *21*, 1197.

[30] (a) Milbrath, D. S.; Verkade, J. G. *J. Am. Chem. Soc.* **1977**, *99*, 6607. (b) Haemers, M.; Ottinger, R.; Zimmermann, D.; Reisse, J. *Tetrahedron Lett.* **1973**, 2241.

[31] Hudson, H. R.; Rees, R. G.; Weekes, J. E. *J. Chem. Soc., Perkin Trans. 1.* **1974**, 982.

[32] Spencer, A.; Werner, H. *J. Organomet. Chem.* **1979**, *171*, 219.

[33] Werner, H. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 927.

$(NO)(PPh_3)Re(OCH_2)Co(PMe_3)(CO)(\eta^5\text{-}C_5H_5)$, might be generated and that the PPh_3 present would trap this adduct by effecting a well-precedented[32] insertion of CO into the cobalt–carbon bond. However, the principal reaction was phosphine exchange to give **6** (64%) and $(\eta^5\text{-}C_5H_5)Co(CO)(PPh_3)$ (65%).

The following nucleophiles did not react with **1**, as assayed by ^{31}P or ^1H NMR: $S(CH_3)_2$ (10.0 equiv, CH_2Cl_2); $PPN^+[Co(CO)_4]^-$ (1.0 equiv, THF);[34] $(\eta^5\text{-}C_5H_5)Co(CO)_2$ (2.0 equiv, acetone-d_6). Grignard reagents failed, under the conditions investigated, to give addition reactions. Complex mixtures of products were obtained when **1** was treated with $P(OMe)_3$ (5.0 equiv, THF) and $NaOCH_3$ (2.0 equiv, THF).

Reactions of **1** with electrophiles were attempted. In the most informative experiment, **1** was dissolved in neat CF_3COOH. Slow decomposition occurred, but a ^1H NMR spectrum recorded after 3 days showed **1** to be <50% consumed. Complex **1** was also treated with methylidene complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)({=}CD_2)]^+PF_6^-$ at -73 °C. The sample was warmed to -10 °C, but no evidence of oxygen atom transfer to give **1**-d_2, or any other reaction between these two complexes, was observed.

Finally, for comparison purposes some related reactions of ethylene complex[24] $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H_2C{=}CH_2)]^+PF_6^-$ were studied. No reaction was observed in CD_3CN over the course of 2 weeks at 56 ± 3 °C. No reaction took place when $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H_2C{=}CH_2)]^+PF_6^-$ was treated with formyl complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CHO)$ at 0 °C (1 h, CH_2Cl_2); at room temperature only a very slow decomposition of the formyl complex occurred. Addition of PPh_3 (2.0 equiv) to an acetone-d_6 solution of $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H_2C{=}CH_2)]^+PF_6^-$ gave 7% conversion to an adduct for which we suggest the structure $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2CH_2PPh_3)]^+ PF_6^-$. Data (acetone-$d_6$): ^1H NMR δ 5.19 (C_5H_5); $^{31}P\{^1H\}$ NMR (ppm, -29 °C) 22.38 (s), 20.22 (s). Addition of more PPh_3 (total of 10.0 equiv) gave a 80:20 ratio of $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H_2C{=}CH_2)]^+PF_6^-$ to the new product.

Discussion

Synthesis and Structure of 1. Equation 1 constitutes the first synthesis of a formaldehyde complex that does not utilize formaldehyde or an oligomeric form thereof. We believe that oxygen atom transfer to methylidene complexes, and likely CH_2 transfer to oxide complexes, will provide a convenient route to many formaldehyde complexes. Recently, M. L. H. Green has found that addition of methanol to a tungsten hydride complex gives the formaldehyde dihydride complex $W(H)_2(PMe_3)_4(\eta^2\text{-}H_2C{=}O)$.[15] This reaction was proposed to occur via an intermediate methoxide complex, and then hydride migration. We similarly find that **1** can be generated from a methoxide complex, $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(OCH_3)$ (**7**), by intermolecular hydride abstraction with $Ph_3C^+PF_6^-$. However, competitive methoxide ligand abstraction also occurs.

Complex **1**, like all other structurally characterized formaldehyde complexes, exhibits a $\eta^2\text{-}H_2C{=}O$ rather than a $\eta^1\text{-}H_2C{=}O$ coordination geometry. Its carbon–oxygen bond length, 1.374 (19) Å, is significantly longer than the C=O double-bond length in free formaldehyde (1.255 Å) and slightly shorter than typical carbon–oxygen single-bond distances (1.41–1.43 Å).[34] Similar formaldehyde complex carbon–oxygen bond lengths have been reported for $Fe(CO)_2(P(OMe)_3)_2(\eta^2\text{-}H_2C{=}O)$ (1.32 (2) Å),[11b] $(\eta^5\text{-}C_5H_5)_2V(\eta^2\text{-}H_2C{=}O)$ (1.353 (10) Å),[12] and $(\eta^5\text{-}C_5H_5)_2Mo(\eta^2\text{-}H_2C{=}O)$ (1.360 (9) Å).[13a] However, the carbon–oxygen bond length in $Os(CO)_2(PPh_3)_2(\eta^2\text{-}H_2C{=}O)$ is significantly longer (1.584 (11) Å).[10a,b]

The HOMO of the $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^+$ fragment is the d orbital shown in Ib above.[36] Figure 3 shows that the $\eta^2\text{-}H_2C{=}O$ ligand adopts a conformation that maximizes overlap of this HOMO with the $H_2C{=}O$ π^* acceptor orbital. Extended Hückel calculations (Figure 4) predict this to be the lowest energy conformation. When the donor–acceptor interaction is removed by rotating the $\eta^2\text{-}H_2C{=}O$ ligand, the HOMO rises in energy and becomes rhenium-centered I and the LUMO falls in energy and takes on substantial $H_2C{=}O$ π^* character. The magnitude of the HOMO energy stabilization in the observed geometry established this overlap as the conformation-determining factor, in accord with Walsh's rule.[37] The lengthened C–O bond in **1** is also a direct consequence of this overlap, and the complex is likely best viewed as a cyclopropane-like oxametallacycle. Although we conducted minimal energy optimization, the $\eta^2\text{-}H_2C{=}O$ rotational barrier calculated in Figure 4 is close to experimental values for olefin rotational barriers in metal complexes.[38]

The $\eta^2\text{-}H_2C{=}O$ ligand in **1** is not bound symmetrically but is "slipped"[39] with rhenium closer to oxygen as illustrated in Figure 3b. This feature is also evident in other structurally characterized formaldehyde complexes. For comparison purposes, we define the degree of slippage as the displacement of point X (Figure 3b) from the midpoint of the C–O bond, *divided* by half the C–O bond length. The $\eta^2\text{-}H_2C{=}O$ slippage in **1** is then 16%, and values in other complexes range from 7% for $Fe(CO)_2(P(OMe)_3)_2(\eta^2\text{-}H_2C{=}O)$[11b] to 25% for $Os(CO)_2(PPh_3)_2(\eta^2\text{-}H_2C{=}O)$.[10b] The direction of slippage—toward the more electronegative terminus—is the same as has been observed in similar complexes of polarized olefins.[39b]

Reactivity of 1. Several interesting reactivity comparisons can be made from the preceding data. Complex **1** is the only cationic formaldehyde complex prepared to date and differs from the neutral formaldehyde complexes described above in undergoing high-yield nucleophilic additions but not well-defined electrophilic additions. This seems a logical consequence of its cationic character, and we predict that other positively charged formaldehyde complexes will behave similarly.

It is also evident that the formaldehyde ligand in **1** undergoes both nucleophilic addition and displacement more readily than the ethylene ligand in $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H_2C{=}CH_2)]^+PF_6^-$. However, it is clear that formaldehyde is not an unusually labile ligand. Our ^1H NMR

---

[34] Gladysz, J. A.; Williams, G. M.; Tam, W.; Johnson, D. L.; Parker, D. W.; Selover, J. C. *Inorg. Chem.* **1979**, *18*, 553.

[35] Streitwieser, A., Jr.; Heathcock, C. H. *Introduction to Organic Chemistry*, 2nd ed.; Macmillan: New York, 1981; p 357; pp 229–230.

[36] Kiel, W. A.; Lin, G.-Y.; Constable, A. G.; McCormick, F. B.; Strouse, C. E.; Eisenstein, O.; Gladysz, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 4865.

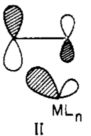
[37] (a) Albright, T. A.; Burdett, J. K.; Whangbo, M.-H. *Orbital Interactions in Chemistry*; Wiley: New York, 1985; p 94. (b) There is another $\eta^2\text{-}H_2C{=}O$ conformation, corresponding to θ = 260° in Figure 4, in which significant overlap of I with the $\eta^2\text{-}H_2C{=}O$ π^* orbital would occur. It is calculated to be 11 kcal/mol less stable. Although this energy difference must be interpreted with caution, we speculate that, since the $\eta^2\text{-}H_2C{=}O$ π^* acceptor orbital has a greater coefficient on carbon, it may be due to a slight asymmetry in I. Also, the $H_2C{=}$ terminus may on steric grounds prefer to be anti to the phosphine.

[38] (a) Albright, T. A. *Acc. Chem. Res.* **1982**, *15*, 149. (b) Mann, B. E. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: New York, 1982; Vol. 3, pp 105–108.

[39] (a) Eisenstein, O.; Hoffmann, R. *J. Am. Chem. Soc.* **1981**, *103*, 4308. (b) Chang, T. C. T.; Foxman, B. M.; Rosenblum, M.; Stockman, C. *Ibid.* **1981**, *103*, 7361.

data bound $\Delta G^{\ddagger}_{373}$ for dissociation as greater than 17.5 kcal/mol. Hence, the scarcity of formaldehyde complexes in the literature may be ascribed to the relatively late development of synthetic methodology.

Eisenstein and Hoffmann recently analyzed the activation of coordinated olefins toward nucleophilic attack using extended Hückel MO theory.[39a] They describe the orbital undergoing attack as essentially olefin π^* with some metal d character added in an antibonding way. Activation results from slippage of the metal toward one C=C terminus, thus localizing the LUMO on the remote carbon, as shown in II.



II

These findings provide a context for rationalizing the greater reactivity of η^2-$H_2C{=}O$ than $H_2C{=}CH_2$ toward nucleophilic attack in $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^2\text{-}H_2C{=}X)]^+PF_6^-$ complexes. First, recall that the asymmetry of the π^* orbital is in part responsible for the greater facility of nucleophilic attack upon free $H_2C{=}O$, as compared to free $H_2C{=}CH_2$. This asymmetry will be present in complexed η^2-$H_2C{=}O$ as well. Second, the η^2-$H_2C{=}O$ slippage observed in the structure of 1 should enhance this effect. Interestingly, 1 is to our knowledge the first heteroolefin complex for which nucleophilic addition has been observed.

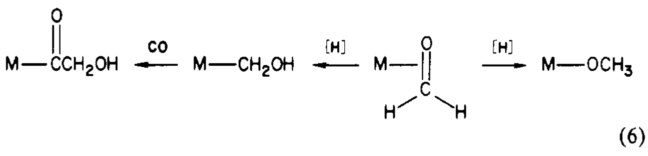
The preceding MO arguments also rationalize the observed regiochemistry of phosphine addition to the η^2-$H_2C{=}O$ ligand in 1 (eq 3). Furthermore, note that carbon attack allows greater separation of the nucleophile from the bulky PPh_3 ligand. Nucleophilic attack upon alkylidene complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(=CHR)]^+PF_6^-$ occurs exclusively from a direction anti to the PPh_3.[36] Also, it is in our opinion likely that eq 3 is under thermodynamic control. It can then be concluded that the sum of the Re–O and H_2C–P bond strengths in 5 and 6 must be greater than the Re–CH_2 and O–P bond strengths in the alternative ReCOP regioisomer. Since phosphorus–carbon bond strengths in phosphines are typically 62–67 kcal/mol and phosphorus–oxygen bond strengths in phosphites are 83–85 kcal/mol,[40] the rhenium–oxygen bonds in 5 and 6 should be at least 20 kcal/mol stronger than analogous rhenium–carbon bonds.

Since $(\eta^5\text{-}C_5H_5)Co(CO)(PPh_3)$ is a better nucleophile than PPh_3 toward CH_3I by an order of magnitude[41] and hence is also likely a better *base* toward carbon, we had expected $(\eta^5\text{-}C_5H_5)Co(CO)(PMe_3)$ to add to the η^2-$H_2C{=}O$ ligand of 1. Instead, only substitution of η^2-$H_2C{=}O$ by the acetone solvent was observed. Of possible relevence, we note that acetone-d_6 effects the displacement of $(\eta^5\text{-}C_5H_5)Co(CO)_2$ from $(\eta^5\text{-}C_5H_5)(CO)_3Mo^+{\leftarrow}Co(CO)_2(\eta^5\text{-}C_5H_5)$, giving $[(\eta^5\text{-}C_5H_5)Mo(CO)_3(\eta^1\text{-}(CD_3)_2C{=}O)]^+$.[42] Also, $(\eta^5\text{-}C_5H_5)Co(CO)(L)$ complexes are capable of redox chemistry,[43] which can promote substitution lability.[44]

The displacement of η^2-$H_2C{=}O$ by iodide ($3 \rightarrow 4$, eq 2) has precedent in the similar displacement of olefins from cationic iron complexes $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(RCH{=}CHR)]^+$ by iodide.[45] We note in passing that major mechanistic questions attend these substitution reactions. In view of the rapidity of $3 \rightarrow 4$, a dissociative mechanism is unlikely.

Formyl complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CHO)$ has been previously shown to be a good hydride donor[20] and is uniquely effective for the preparative reduction of formaldehyde complex 1 to methoxide complex 7 (eq 4). We believe that it is critical to generate 7 in the *absence* of Lewis acid byproducts such as those accompanying borohydride reductions. Formyl complexes are believed to be intermediates in the conversion of CO/H_2 to oxygenated organic products over many homogeneous catalysts.[6,7] Hence, eq 4 suggests an intriguing possible pathway for the generation of catalyst-bound methoxide ligands. Methoxide complexes are of particular current interest,[46] and the chemical properties of 7—which is extremely labile—are under study. At present, we call attention to the sharp IR band at 2763 cm^{-1} (Figure 5). This absorbance, which has been observed in at least two other methoxide complexes,[47] is likely a $\nu_{C\text{-}H}$ that is unique to methoxide ligands. Comparable bands have been noted in IR spectra of surface-bound methoxides.[48]

As indicated above, η^2-$H_2C{=}O$ intermediates are believed to control methanol/glycol product distributions in some metal-catalyzed CO/H_2 reactions.[6,7] It has been proposed, as outlined in eq 6, that catalyst systems that generate acidic metal hydride intermediates convert the η^2-$H_2C{=}O$ ligand to a hydroxymethyl (CH_2OH) ligand and systems that generate less acidic metal hydride intermediates convert the η^2-$H_2C{=}O$ ligand to a methoxide ligand.[6] The former can be elaborated to glycol products and the latter to methanol and derivatives thereof. The regiochemistry of proton/hydride addition to isolated formaldehyde complexes corroborates this hypothesis. Protonation of $Os(CO)_2(PPh_3)_2(\eta^2\text{-}H_2C{=}O)$[10b] and $Fe(CO)_2(P(OMe)_3)_2(\eta^2\text{-}H_2C{=}O)$[11b] leads in both cases to hydroxymethyl complexes. In contrast, reaction of 1 with suitable *hydride* sources gives methoxide complex 7.



$$M\text{—}\overset{O}{\overset{\|}{C}}CH_2OH \xleftarrow{CO} M\text{—}CH_2OH \xleftarrow{[H]} M\text{—}\underset{H\ \ H}{\overset{O}{\overset{\|}{C}}} \xrightarrow{[H]} M\text{—}OCH_3 \qquad (6)$$

Summary

Our preparation of $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^2\text{-}H_2C{=}O)]^+PF_6^-$ (1) illustrates a new and potentially general strategy for the synthesis of formaldehyde complexes. The η^2-$H_2C{=}O$ conformation in 1 is accurately predicted by Hückel MO calculations. We have discovered the first examples of nucleophilic addition to coordinated formaldehyde—reactions that may have relevance to catalytic reactions involving coordinated formaldehyde intermedi-

---

(40) Bentrude, W. G. In *Free Radicals*; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. 2, pp 598–600.

(41) Pearson, R. G.; Figdore, P. E. *J. Am. Chem. Soc.* **1980**, *102*, 1541.

(42) Sünkel, K.; Nagel, U.; Beck, W. *J. Organomet. Chem.* **1983**, *251*, 227.

(43) (a) McKinney, R. J. *Inorg. Chem.* **1982**, *21*, 2051. (b) Boncella, J. M.; Andersen, R. A. *J. Chem. Soc., Chem. Commun.* **1984**, 809.

(44) Zizelman, P. M.; Amatore, C.; Kochi, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 3771.

(45) (a) Cutler, A.; Ehntholt, D.; Giering, W. P.; Lennon, P.; Raghu, S.; Rosan, A.; Rosenblum, M.; Tancrede J.; Wells, D. *J. Am. Chem. Soc.* **1976**, *98*, 3495. (b) Laycock, D. E.; Hartgerink, J.; Baird, M. C. *J. Org. Chem.* **1980**, *45*, 291.

(46) (a) Rees, W. M.; Atwood, J. D. *Organometallics* **1985**, *4*, 402. (b) Bryndza, H. *Ibid.* **1985**, *4*, 406. (c) Bryndza, H. E.; Kretchmar, S. A.; Tulip, T. E. *J. Chem. Soc., Chem. Commun.* **1985**, 977. (d) Anderson, A. B.; Ray, N. K. *J. Am. Chem. Soc.* **1985**, *107*, 253. (e) see also Chisholm, M. H.; Folting, K.; Heppert, J. A.; Hoffman, D. M.; Huffman, J. C. *Ibid.* **1985**, *107*, 1234.

(47) (a) Cameron, T. S.; Grundy, K. R.; Robertson, K. N. *Inorg. Chem.* **1982**, *21*, 4149. (b) McCarron, E. M., III; Staley, R. H.; Sleight, A. W. *Ibid.* **1984**, *23*, 1043.

(48) (a) Liu, H.-F.; Liu, R.-S.; Liew, K. Y.; Johnson, R. E.; Lunsford, J. H. *J. Am. Chem. Soc.* **1984**, *106*, 4117. (b) Groff, R. P. *J. Catal.* **1984**, *86*, 215. (c) Lavalley, J.-C.; Lamotte, J.; Busca, G.; Lorenzelli, V. *J. Chem. Soc., Chem. Commun.* **1985**, 1006. (c) See also: Park, M.; Hauge, R. H.; Kafafi, Z. H.; Margrave, J. L. *Ibid.* **1985**, 1570.

ates. The synthesis, structure, and reactivity of related aldehyde and ketone complexes will be reported in the near future.

Experimental Section

General Data. All reactions were carried out under a dry N_2 atmosphere. IR spectra were recorded on a Perkin-Elmer 1500 (FT) spectrometer. All ^1H and ^{13}C NMR spectra were recorded on modern 200–300 MHz spectrometers and were referenced to internal $(CH_3)_4Si$. All ^{31}P NMR spectra were recorded on Varian FT-80A and XL-300 spectrometers and were referenced to external H_3PO_4. Mass spectra were obtained on a VG 770 spectrometer. Microanalyses were conducted by Galbraith and Schwarzkopf Laboratories. Melting points were determined in evacuated capillaries and were not corrected.

Solvents were purified as follows: acetone, distilled from $CaSO_4$; CH_2Cl_2 and $CHCl_3$, distilled from P_2O_5; benzene and ether, distilled from Na/benzophenone; hexane, distilled from Na; CH_3OH, dried over $CaSO_4$ and purged with N_2; CD_3CN and CD_2Cl_2, vacuum transferred from CaH_2; acetone-d_6, vacuum transferred from $CaSO_4$; $CDCl_3$, vacuum transferred from P_2O_5; Me_2SO-d_6, dried over CaH_2 and distilled under 10^{-3} torr; $CDCl_2CDCl_2$ (KOR, Inc.), purged with N_2; CF_3CO_2H, distilled from P_2O_5.

Reagents were obtained as follows: $Ph_3C^+PF_6^-$, purchased from Aldrich or Columbia Organics and purified by precipitation from CH_2Cl_2/benzene or CH_2Cl_2/ethyl acetate; $C_6H_5I^+$–O^-, prepared from iodosobenzene diacetate by a literature procedure;[49] PPh_3, purchased from Pressure Chemical and recrystallized from ethanol; PMe_3 and (η^5-C_5H_5)Co$(CO)_2$, used as received from Strem Chemicals; (η^5-C_5H_5)Co(CO)(PMe_3) and (η^5-C_5H_5)Co(CO)(PPh_3), prepared by literature procedures;[32,50] NaI, $NaOCH_3$, and *p*-$CH_3C_6H_4SO_3H \cdot H_2O$, used as received from Malinckrodt, Aldrich, and MCB, respectively; Ph_3SiCH_3, prepared from CH_3MgBr and Ph_3SiCl similarly to a literature procedure[51] and then recrystallized from cold CH_3OH and sublimed in vacuo at 110 °C. An authentic sample of Ph_3COCH_3 was obtained from Pfaltz & Bauer.

Preparation of [(η^5-C_5H_5)Re(NO)(PPh_3)(η^2-$H_2C{=}O$)]$^+PF_6^-$ (1). A Schlenk flask was charged with (η^5-C_5H_5)Re(NO)(PPh_3)(CH_3) (0.500 g, 0.896 mmol),[20] CH_2Cl_2 (150 mL), and a stir bar. The solution was cooled to −78 °C and stirred, and $Ph_3C^+PF_6^-$ (0.382 g, 0.986 mmol) was added. After 15 min, $C_6H_5I^+$–O^- (0.492 g, 2.24 mmol) was added. The resulting suspension was kept at −23 °C for 3 h, then filtered, and concentrated to ca. 75 mL by rotary evaporation. Hexane was added, giving a precipitate. This was collected by filtration and dried to give 1 (0.533 g, 0.742 mmol, 83%) as a cream-colored solid. Crystallization from CH_2Cl_2/hexanes afforded bronze air-stable crystals of 1 that were dried in vacuo; mp 163–175 °C dec. Anal. Calcd for $C_{24}H_{22}F_6NO_2P_2Re$: C, 40.11; H, 3.09; N, 1.95; P, 8.62. Found: C, 39.83; H, 3.16; N, 1.88; P, 8.12.

Preparation of [(η^5-C_5H_5)Re(NO)(PPh_3)(CD_3CN)]$^+PF_6^-$ (2-d_3) from 1. The following experiment is representative. A 5-mm NMR tube was charged with 1 (0.065 g, 0.091 mmol), Ph_3SiCH_3 standard (0.050 g, 0.182 mmol), and CD_3CN (0.500 mL). The mixture was kept at room temperature and periodically monitored by ^1H NMR. After 18 days, 2-d_3 was present in 92% yield vs. the standard. Solvent was evaporated under a N_2 stream, and the residue was crystallized from $CHCl_3$/ether. This gave yellow needles of 2-d_3 (0.044 g, 0.061 mmol, 67%): IR (cm^{-1}, CH_2Cl_2) $\nu_{N{\equiv}O}$ 1709 s; ^1H NMR (δ, $CDCl_3$) 5.53 (s, 5 H) (lit.[24] δ 5.53).

Preparation of [(η^5-C_5H_5)Re(NO)(PPh_3)(η^2-$H_2C{=}O$)]$^+I^-$ (3). A Schlenk flask was charged with 1 (0.200 g, 0.279 mmol), acetone (10 mL), and a stir bar. Then NaI (0.209 g, 1.39 mmol) was added with stirring. A precipitate rapidly formed that was collected by filtration, washed with acetone (2 × 5 mL) and ether (2 × 10 mL), and dried in vacuo. This gave 3 (0.133 g, 0.190 mmol, 68%) as a cream-colored powder, mp 138–184 °C dec (gradual). Anal. Calcd for $C_{24}H_{22}INO_2PRe$: C, 41.15; H, 3.17; I, 18.12. Found: C, 41.14; H, 3.16; I, 18.29.

Preparation of (η^5-C_5H_5)Re(NO)(PPh_3)(I) (4) from 3. A Schlenk flask was charged with 3 (0.100 g, 0.143 mmol), CH_3OH (3 mL), and a stir bar. The solution was stirred and turned faint orange (<5 min). A purple solid precipitated. Then CH_2Cl_2 (1 mL) was added, generating a deep red solution. The reaction mixture was filtered, and ether was added to the filtrate by vapor diffusion. This gave deep purple crystals of 4 (0.062 g, 0.093 mmol, 65%): IR (cm^{-1}, $CHCl_3$) $\nu_{N{\equiv}O}$ 1677 s; ^1H NMR (δ, $CDCl_3$) 5.20 (s, 5 H); $^{31}P\{^1H\}$ NMR (ppm, acetone) 12.96 (s) (lit.[26] 1677 cm^{-1}; δ 5.19; 12.85 ppm).

Preparation of [(η^5-C_5H_5)Re(NO)(PPh_3)(OCH_2PPh_3)]$^+PF_6^-$ (5). A 20 mL wide-mouth vial was charged with 1 (0.104 g, 0.145 mmol), PPh_3 (0.076 g, 0.290 mmol), and CH_2Cl_2 (2 mL). Then ether was introduced into the resulting solution by vapor diffusion. This gave orange-red needles of 5 (0.127 g, 0.130 mmol, 89%) that were washed with ether and dried in vacuo; mp 175–176 °C dec. Anal. Calcd for $C_{42}H_{37}F_6NO_2P_3Re$: C, 51.43; H, 3.80; N, 1.43; P, 9.47. Found: C, 51.66; H, 3.77; N, 1.52; P, 9.39.

Preparation of [(η^5-C_5H_5)Re(NO)(PPh_3)(OCH_2PMe_3)]$^+$-$PF_6^- \cdot CH_2Cl_2$ (6·CH_2Cl_2). A Schlenk flask was charged with 1 (0.100 g, 0.139 mmol), CH_2Cl_2 (2 mL), and a stir bar and was cooled to 0 °C. Then PMe_3 (15 μL, 11 mg, 0.14 mmol) was added with stirring. The orange solution was warmed to room temperature, and ether was introduced by vapor diffusion. This gave orange-red crystals of 6·CH_2Cl_2 (0.104 g, 0.118 mmol, 85%) that were washed with ether and dried in vacuo, mp 121–126 °C dec. Anal. Calcd for $C_{27}H_{31}F_6NO_2P_3Re \cdot CH_2Cl_2$: C, 38.24; H, 3.78; Cl, 8.06. Found: C, 38.46; H, 3.87; Cl, 7.85.

Preparation of (η^5-C_5H_5)Re(NO)(PPh_3)(OCH_3) (7). A. A Schlenk flask was charged with (η^5-C_5H_5)Re(NO)(PPh_3)(CH_3)[20] (0.586 g, 1.05 mmol), *p*-$CH_3C_6H_4SO_3H \cdot H_2O$ (0.598 g, 3.15 mmol), CH_3OH (200 mL), and a stir bar. The solution was stirred and rapidly turned (<5 min) deep orange as (η^5-C_5H_5)Re(NO)(PPh_3)(OSO_2-*p*-$C_6H_4CH_3$) was generated.[27] Then $NaOCH_3$ (0.680 g, 12.6 mmol) was added. This gave a light orange solution within 30 min. After 6 h, solvent was removed in vacuo leaving an orange solid that was extracted with benzene (ca. 50 mL). The extract was filtered and concentrated to ca. 20 mL by rotary evaporation. Hexane was added, and a salmon precipitate formed and was collected by filtration and dried (0.542 g, 0.944 mmol). A second crop was obtained from the filtrate for a total of 0.561 g (0.977 mmol, 93%) of crude 7. Deep red crystals of 7, mp 137–163 °C dec, were obtained from C_6H_6/hexanes and dried in vacuo. Anal. Calcd for $C_{24}H_{23}NO_2PRe$: C, 50.16; H, 4.03; N, 2.44; P, 5.39. Found: C, 50.23; H, 4.03; N, 2.51; P, 5.32. Mass spectrum (15 eV): *m/e* (relative intensity) 575 ($M^+ - {}^{187}Re$, 5), 313 ($M^+ - PPh_3$, 2), 262 (Ph_3P^+, 100). **B.** A 5-mm NMR tube was charged with 1 (0.025 g, 0.035 mmol), formyl complex (η^5-C_5H_5)Re(NO)(PPh_3)(CHO)[20] (0.020 g, 0.035 mmol), and Ph_3SiCH_3 standard (0.019 g, 0.069 mmol) and was capped with a septum. The tube was placed in liquid N_2, and CD_2Cl_2 (0.500 mL) was added by syringe. The mixture was freeze–thaw degassed at −78 °C and warmed to room temperature. Analysis by ^1H NMR indicated the formation of [(η^5-C_5H_5)Re(NO)(PPh_3)(CO)]$^+PF_6^-$ (δ 5.78 (5 H)) and 7 (δ 3.94 (3 H)) in 99% and 74% yields relative to the standard (δ 0.82). **C.** A Schlenk flask was charged with 1 (0.150 g, 0.209 mmol), CH_2Cl_2 (20 mL), and a magnetic stir bar. The flask was cooled to −78 °C, and (η^5-C_5H_5)Re(NO)(PPh_3)(CHO) (0.120 g, 0.209 mmol) was added. This gave a yellow slurry. The cold bath was removed, and the mixture was allowed to warm to room temperature. Solvent was removed from the resulting red homogeneous solution in vacuo, and the solid residue was extracted with C_6H_6 (ca. 10 mL). The yellow solid remaining was collected by filtration, washed with C_6H_6 (ca. 2 mL), and dried to give [(η^5-C_5H_5)Re(NO)(PPh_3)(CO)]$^+PF_6^-$ (0.136 g, 0.190 mmol, 91%): IR (cm^{-1}, KBr) $\nu_{C{\equiv}O}$ 2020 s, $\nu_{N{\equiv}O}$ 1755 s (lit:[20] 2017, 1765 cm^{-1}). The red benzene filtrate from above was concentrated to ca. 5 mL by rotary evaporation. Hexane (ca. 3 mL) was added, and a floculent tan decomposition product was removed by filtration. The filtrate was again concentrated, and addition of hexanes gave 7 (0.062 g, 0.108 mmol, 52%) as a salmon-colored precipitate.

Reaction of 7 with $Ph_3C^+PF_6^-$. A 5-mm NMR tube was charged with $Ph_3C^+PF_6^-$ (0.013 g, 0.034 mmol), Ph_3SiCH_3 standard (0.010 g, 0.036 mmol), and CD_2Cl_2 (0.250 mL) and was capped with a septum and then cooled to −78 °C. A solution of 7 (0.020 g, 0.035 mmol) in CD_2Cl_2 (0.300 mL) was added by syringe, and

---

(49) Saltzman, H.; Sharefkin, J. G. *Organic Synthesis*; Wiley: New York, 1973; Collect. Vol. V, p 658.

(50) King, R. B. *Inorg. Chem.* **1966**, *5*, 82.

(51) Marsden, H.; Kipping, F. S. *J. Chem. Soc.* **1908**, *93*, 198.

the tube was placed in a −70 °C NMR probe. A ^1H NMR spectrum showed that all **7** had been consumed, and the $\eta^5\text{-}C_5H_5$ resonance of **1** (δ 5.98; 20%) was present. Unassigned major $\eta^5\text{-}C_5H_5$ (δ 4.41) and OCH_3 (δ 2.91; ca. 50%) resonances were also present, as well as minor $\eta^5\text{-}C_5H_5$ resonances (δ 5.8–5.4). All resonances were broadened. The probe was warmed, and resonances sharpened. Those at δ 4.41 and 2.91 disappeared, and a resonance for Ph_3COCH_3 (δ 3.01) appeared. At room temperature, **1** and Ph_3COCH_3 were present in 15% of 42% yields, respectively.

Reaction of 1 with $(\eta^5\text{-}C_5H_5)Co(CO)(PMe_3)$. A 5-mm NMR tube was charged with **1** (0.025 g, 0.035 mmol), $(\eta^5\text{-}C_5H_5)Co(CO)(PMe_3)$ (0.008 g, 0.035 mmol), Ph_3SiCH_3 standard (0.010 g, 0.036 mmol), and acetone-d_6 (0.450 mL). The tube was kept at room temperature for 16 h. Subsequent ^1H NMR analysis showed a new $\eta^5\text{-}C_5H_5$ resonance (δ 5.81 (s); 58%) that was assigned to $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^1\text{-}(CD_3)_2C{=}O)]^+PF_6^-$ (**8**-d_6). Complex $(\eta^5\text{-}C_5H_5)Co(CO)(PMe_3)$ was still present (69%). IR (cm^{-1}, thin film): $\nu_{C{\equiv}O}$ 1906 s (CoCO), $\nu_{N{\equiv}O}$ 1686 s (**8**-d_6), $\nu_{C{=}O}$ 1617 m (**8**-d_6). $^{31}P\{^1H\}$ NMR (ppm, acetone-d_6, −30 °C): 17.35 (s, **8**-d_6). Lit. (authentic **8**):[22] IR (cm^{-1}, thin film) 1687 s, 1621 m; ^1H NMR (δ, acetone-d_6) 5.84 (s, 5 H); $^{31}P\{^1H\}$NMR (ppm, acetone-d_6, −30 °C) 17.55 (s).

Reaction of 5 with $(\eta^5\text{-}C_5H_5)Co(CO)(PMe_3)$. A 5-mm NMR tube was charged with **5** (0.034 g, 0.035 mmol), $(\eta^5\text{-}C_5H_5)Co(CO)(PMe_3)$ (0.008 g, 0.035 mmol), Ph_3SiCH_3 standard (0.010 g, 0.036 mmol), and acetone-d_6 (0.400 mL). The tube was kept at room temperature for 16 h. Subsequent ^1H NMR analysis of the $\eta^5\text{-}C_5H_5$ resonances showed **6** (64%), $(\eta^5\text{-}C_5H_5)Co(CO)(PPh_3)$ (δ 4.65 (d, J_{HP} = 1.1 Hz); 65%), remaining $(\eta^5\text{-}C_5H_5)Co(CO)(PMe_3)$ (30%), and **8**-d_6 (8%). These assignments were verified: $^{31}P\{^1H\}$ NMR (ppm, −30 °C) 21.84, 18.29 (s, **6**), 68.2 (vbr s, $(\eta^5\text{-}C_5H_5)Co(CO)(PPh_3)$), 17.36 (s, **8**-$d_6$); IR (cm^{-1}, thin film) $\nu_{C{\equiv}O}$ 1921 s ($(\eta^5\text{-}C_5H_5)Co(CO)(PPh_3)$). Data under identical conditions for authentic $(\eta^5\text{-}C_5H_5)Co(CO)(PPh_3)$:[50] IR $\nu_{C{\equiv}O}$ 1924 s; ^1H NMR δ 4.65 (d, J_{HP} = 0.9 Hz, 5 H); $^{31}P\{^1H\}$ NMR 67.4 ppm (vbr s).

Attempted Reaction of 1 with $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)({=}CD_2)]^+PF_6^-$. A 5-mm NMR tube was charged with $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)({=}CD_2)]^+PF_6^-$ (0.020 g, 0.029 mmol), capped with a septum, and cooled to −78 °C. Then CD_2Cl_2 (0.500 mL) and **1** (0.021 g, 0.029 mmol) in CD_2Cl_2 (0.500 mL) were added by syringe. The tube was transferred to a −73 °C NMR probe, and ^1H NMR spectra were recorded as the probe was warmed to −10 °C in increments. No evidence for oxygen atom transfer product $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)({=}CH_2)]^+PF_6^-$ was observed.

X-ray Crystal Structure of 1. X-ray data were collected as described in Table II on a Syntex P$\bar{1}$ automated diffractometer using techniques previously described.[52] Of 4847 unique reflections collected with $2\theta < 50°$, 4090 with $I > 3\sigma(I)$ were used in the final refinement.

The rhenium positions were obtained from a three-dimensional Patterson map. Several cycles of full-matrix refinement followed by the computation of a three-dimensional difference map yielded all non-hydrogen atoms. Absorption corrections were applied and the rhenium, phosphorus, and fluorine atoms were refined with anisotropic thermal parameters. Other atoms were refined isotropically. Anomalous dispersion corrections were applied throughout the refinement. The formaldehyde C and O atoms were distinguished by first assigning both to be N atoms for one refinement cycle. The atom with the larger apparent thermal parameter was tentatively assigned to be C, and the atom with the smaller apparent thermal parameter was assigned to be O. A refinement cycle was then completed, followed by another cycle with the C and O assignments reversed. The R value for the former cycle was lower, confirming the assignment. The positions of the nonformaldehyde hydrogen atoms were calculated, the C–H bond distances were set at 1.00 Å with idealized sp^2 geometry, and isotropic thermal parameters were assigned. The formaldehyde hydrogens could not be located.

Two overlapping sets of peaks for the NO and $\eta^2\text{-}H_2C{=}O$ N, C, and O atoms were found in the electron density map for *one* of the two non-symmetry-related rhenium cations. To incorporate this disorder, the isotropic thermal parameters of the disordered atoms were constrained to equal those of the corresponding atoms in the nondisordered rhenium cation. The site occupancies of the disordered atoms were allowed to refine with the constraint that the sum of fractional occupancies for each disordered atom equaled one. All data are taken from the nondisordered rhenium cation.

MO Calculations. Extended Hückel calculations[53] were conducted with weighted H_{ij} formula. The rhenium and phosphorus atoms of model compound $[(\eta^5\text{-}C_5H_5)Re(NO)(PH_3)(\eta^2\text{-}H_2C{=}O)]^+$ were assigned idealized octahedral and tetrahedral geometries, respectively. The $\eta^2\text{-}H_2C{=}O$ carbon and oxygen atoms were assigned bond lengths (below) and angles based upon the X-ray crystal structure determination of **1**. The C–Re–O angle was bisected by an axis perpendicular to the Re–P and Re–N vectors. The $\eta^2\text{-}H_2C{=}O$ ligand was rotated about this axis while the $\overline{\text{Re–O–C}}$ bond distances and angles were held constant. The axis intersected the C–O bond at a distance of 0.699 Å from carbon. The $\eta^2\text{-}H_2C{=}O$ hydrogen atoms were positioned such that the H–C–H plane was normal to the $\overline{\text{Re–O–C}}$ plane and formed an angle of 166.2° with the C–O vector, thus tilting the $\eta^2\text{-}H_2C{=}O$ hydrogen atoms ca. 14° from ideal sp^2 geometry. A similar tilting was noted in the X-ray crystal structure of thioformaldehyde complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^2\text{-}H_2C{=}S)]^+PF_6^-$[14] and in the crystal structures of other formaldehyde complexes.[12,13] The $\overline{\text{Re–O–C}}$ plane bisected the H–C–H angle. Steric interactions with PH_3 were minimized by rotating the Re–P bond to the energy minimum in the conformation θ = 220° (Figure 4). This PH_3 geometry was subsequently used in all values of θ. Bond lengths used for $\eta^2\text{-}CH_2{=}O$ were as follows (Å): Re—C, 2.108; Re—O, 2.036; C—O, 1.375; C—H, 1.090. The remaining bond lengths and H_{ii} and ζ parameters were the same as previously employed.[54]

Acknowledgment. We are grateful to the Department of Energy for support of this research. FT NMR spectra were obtained on instruments acquired via NSF departmental instrumentation grants. W.E.B. thanks the Regents of the University of California for a Fellowship.

Registry No. **1**, 84369-16-4; **2**-d_3, 100815-20-1; **3**, 100815-21-2; **4**, 92695-34-6; **5**, 84369-22-2; **6**, 100815-23-4; **7**, 84369-20-0; **8**-d_6, 100815-25-6; $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3)$, 71763-18-3; $C_6H_5I^+O^-$, 536-80-1; $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CHO)$, 70083-74-8; $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CO)]^+PF_6^-$, 79919-50-9; $(\eta^5\text{-}C_5H_5)Co(CO)(PMe_3)$, 66652-86-6; $(\eta^5\text{-}C_5H_5)Co(CO)(PPh_3)$, 12203-85-9; $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)({=}CD_2)]^+PF_6^-$, 100815-27-8.

---

(52) (a) Strouse, J.; Layten, S. W.; Strouse, C. E. *J. Am. Chem. Soc.* **1977**, *99*, 562. (b) Merrifield, J. H.; Strouse, C. E.; Gladysz, J. A. *Organometallics* **1982**, *1*, 1204.

(53) (a) Hoffmann, R. *J. Chem. Phys.* **1963**, *39*, 1397. (b) Hoffmann, R.; Lipscomb, W. N. *Ibid.* **1962**, *36*, 2179; **1962**, *37*, 2872.

(54) Georgiou, S.; Gladysz, J. A. *Tetrahedron* **1986**, *42*, 1109.