tions/parameter = 7.8).[42] The fractional coordinates and thermal parameters are listed in Table III.

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(42) $R = \sum||F_o| - |F_c||/(\sum|F_o|)$; $R_w = \{\sum w|F_o| - |F_c|)^2/(\sum w|F_o|^2\}^{1/2}$.

Registry No. 1, 108969-10-4; 2, 108969-11-5; 3, 108969-12-6; 4, 108969-13-7; 5, 108969-14-8; 6, 109011-04-3; 7, 108969-15-9; 8, 108969-16-0; 9, 108969-17-1; 10, 108969-18-2; 11, 108969-19-3; 12, 71265-76-4; (dmCh)H, 33482-80-3; (dmCh)K, 82360-21-2; (dmCh)2, 108947-34-8; $TiCl_3(THF)_3$, 18039-90-2; $TiCl_4(THF)_2$, 31011-57-1; $CrCl_2(THF)_2$, 15604-50-9; $FeCl_2(THF)_2$, 70317-90-7; VCl_3, 7718-98-1; $MnCl_2$, 7773-01-5; $FeCl_2$, 7758-94-3; 5,5-dimethyl-1,3-cyclohexanedione, 126-81-8; 5,5-dimethyl-1,3-cyclohexanediol, 597-98-8; 1,4-cyclohexadiene, 628-41-1.

Supplementary Material Available: Tables of bond distances, bond angles, fractional coordinates, thermal parameters, and least-squares planes calculations (11 pages); a listing of observed and calculated structure factors (8 pages). Ordering information is given on any current masthead page.

Crystallographic and Theoretical Analyses of the Structures of Rhenium Formyl and Acyl Complexes of the Formula $(\eta^5\text{-}C_5H_5)Re(NO)(PR_3)(COR')$

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X-ray crystal structures of formyl complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CHO)$ (1) and acyl complex (*SR*,-*RS*)-$(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(COCH(CH_3)CH_2C_6H_5)\cdot(THF)_{0.5}$ ($2\cdot(THF)_{0.5}$) are reported. Crystal data: 1, monoclinic, $P2_1/c$, a = 8.065 (3) Å, b = 15.156 (3) Å, c = 16.896 (4) Å, β = 95.44 (2)°, Z = 4; $2\cdot(THF)_{0.5}$, triclinic, $P\bar{1}$, a = 17.844 (4) Å, b = 11.101 (2) Å, c = 9.704 (2) Å, α = 64.62 (2)°, β = 75.55 (2)°, γ = 73.20 (2)°, Z = 2. Extended Hückel MO calculations on model compounds $(\eta^5\text{-}C_5H_5)Re(NO)(PH_3)(COR)$ predict that the ON–Re–C_α–O torsion angle (θ) should be near 0° or 180°, so that overlap of the rhenium fragment HOMO with the C=O π^* orbital will be maximized. Accordingly, Re–C_α conformations with θ near 180° are found in 1 and $2\cdot(THF)_{0.5}$. This places the C=O oxygen anti to the NO ligand. The geometries of the formyl and acyl ligands are contrasted and compared to those of other formyl and acyl complexes.

Introduction

While metal formyl complexes (L_nMCHO) and acyl complexes (L_nMCOR) have many physical similarities, they exhibit strikingly different chemical properties.[3] The former are good hydride ($H:^-$)[3–5] and hydrogen atom ($H\cdot$)[6] donors, whereas the latter are not ready sources of carbanions ($R:^-$) or alkyl radicals ($R\cdot$). Formyl complexes are generally thermodynamically unstable with respect to hydride complexes (L_nMH) and carbon monoxide,[3,7,8] whereas most acyl complexes are stable with respect to alkyl complexes (L_nMR) and carbon monoxide.[7a,d,9] These contrasting properties are of interest in that both types of complexes play an important role in catalytic CO/H_2 chemistry. For example, formyl complexes are highly probable intermediates in the homogeneously catalyzed conversion of CO/H_2 to oxygenates.[10] Acyl complexes are

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(3) Gladysz, J. A. *Adv. Organomet. Chem.* **1982**, *20*, 1.
(4) (a) Casey, C. P.; Neumann, S. M. *J. Am. Chem. Soc.* **1978**, *100*, 2544. (b) Casey, C. P.; Andrews, M. A.; McAlister, D. R.; Rinz, J. E. *Ibid.* **1980**, *102*, 1927.
(5) (a) Tam, W.; Lin, G.-Y.; Wong, W.-K.; Kiel, W. A.; Wong, V. K.; Gladysz, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 141. (b) Tam, W.; Lin, G.-Y.; Gladysz, J. A. *Organometallics* **1982**, *1*, 525. (c) Tam, W.; Marsi, M.; Gladysz, J. A. *Inorg. Chem.* **1983**, *22*, 1413.
(6) (a) Narayanan, B. A.; Amatore, C.; Casey, C. P.; Kochi, J. K. *J. Am. Chem. Soc.* **1983**, *105*, 6351. (b) Sumner, C. E.; Nelson, G. O. *Ibid.* **1984**, *106*, 432. (c) Narayanan, B. A.; Amatore, C. A.; Kochi, J. K. *Organometallics* **1984**, *3*, 802. (d) Paonessa, R. S.; Thomas, N. C.; Halpern, J. *J. Am. Chem. Soc.* **1985**, *107*, 4333. (e) Barratt, D. S.; Cole-Hamilton, D. J. *J. Chem. Soc., Chem. Commun.* **1985**, 458.
(7) (a) Connor, J. A.; Zafarani-Moattar, M. T.; Bickerton, J.; El Saied, N. I.; Suradi, S.; Carson, R.; Al Takhin, G.; Skinner, H. A. *Organometallics* **1982**, *1*, 1166. (b) Dedieu, A.; Nakamura, S. *J. Organomet. Chem.* **1984**, *260*, C63. (c) Lane, K. R.; Sallans, L.; Squires, R. R. *Organometallics* **1985**, *4*, 408. (d) Nolan, S. P.; Lopez de la Vega, R.; Hoff, C. D. *J. Am. Chem. Soc.* **1986**, *108*, 7852.
(8) For exceptions, see: (a) Wayland, B. B.; Woods, B. A. *J. Chem. Soc., Chem. Commun.* **1981**, 700. (b) Wayland, B. B.; Woods, B. A.; Pierce, R. *J. Am. Chem. Soc.* **1982**, *104*, 302. (c) Moloy, K. G.; Marks, T. J. *Ibid.* **1984**, *106*, 7051.
(9) Casey, C. P.; Bunnell, C. A.; Calabrese, J. C. *J. Am. Chem. Soc.* **1976**, *98*, 1166.
(10) (a) Masters, C. *Adv. Organomet. Chem.* **1979**, *17*, 61. (b) Muetterties, E. L.; Stein, J. *Chem. Rev.* **1979**, *79*, 479. (c) Rofer-DePoorter, C. K. *Ibid.* **1981**, *81*, 447. (d) Blackborow, J. R.; Daroda, R. J.; Wilkinson, G. *Coord. Chem. Rev.* **1982**, *43*, 17. (e) Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 117. (f) Henrici-Olivé, G.; Olivé, S. *J. Mol. Catal.* **1983**, *18*, 367. (g) Dombek, B. D. *Adv. Catal.* **1983**, *32*, 325. (h) See also: Saussey, J.; Lavalley, J. C.; Rais, T.; Chakor-Alami, A.; Hinderman, J. P.; Kiennemann, A. *J. Mol. Catal.* **1984**, *26*, 159.

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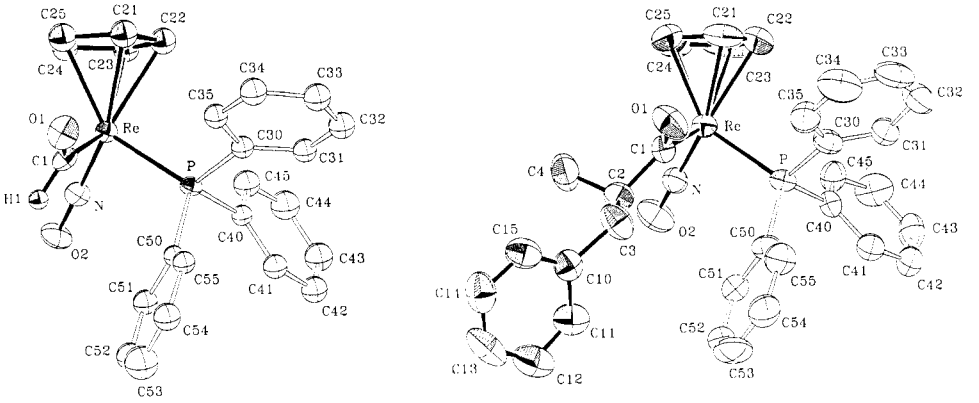
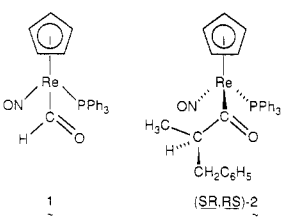


Figure 1. Molecular structures and atomic numbering of (η^5-C_5H_5)Re(NO)(PPh_3)(CHO) (**1**) and (*SR,RS*)-(η^5-C_5H_5)Re(NO)-(PPh_3)(COCH(CH_3)$CH_2C_6H_5$)·$(THF)_{0.5}$ (**2**·$(THF)_{0.5}$).

key intermediates in olefin hydroformylation, the carbonylation of methanol to acetic acid and probably some reactions that give $\geq C_2$ products from CO/H_2.[11]

Structural data have been available for many corresponding aldehydes and ketones for some time.[12] However, there have only been two previous studies, the first by Casey[13] and the second by Berke,[14] in which the structures of corresponding formyl and acyl complexes have been compared. In 1979, we communicated the first X-ray crystal structure of a formyl complex, (η^5-C_5H_5)-Re(NO)(PPh_3)(CHO) (**1**).[15] More recently, we reported the X-ray crystal structure of acyl complex (*SR,RS*)-(η^5-C_5H_5)Re(NO)(PPh_3)(COCH(CH_3)$CH_2C_6H_5$)·$(THF)_{0.5}$ (**2**·$(THF)_{0.5}$).[16] In this full paper, we compare the structural features of these two complexes, and the Re–C_α conformations observed with those predicted by extended Hückel molecular orbital (EHMO) calculations. To facilitate discussion, θ will be used to represent the ON–Re–C_α–O torsion angle.



Results

Complexes **1** and **2** were prepared as described previously.[5a,16] Slow diffusion of petroleum ether (bp 30–50 °C) into a THF solution of **1** gave crystals suitable for X-ray analysis. A THF solution of **2** was layered with hexanes. This gave crystals of the solvate **2**·$(THF)_{0.5}$. X-ray data were obtained as summarized in Table I.

Table I. Summary of Crystallographic Data for (η^5-C_5H_5)Re(NO)(PPh_3)(CHO) (1) and (*SR,RS*)-(η^5-C_5H_5)Re(NO)(PPh_3)(COCH(CH_3)$CH_2C_6H_5$)·$(THF)_{0.5}$ (2·$(THF)_{0.5}$)

	1	2·$(THF)_{0.5}$
mol formula	$C_{24}H_{21}NO_2PRe$	$C_{33}H_{31}NO_2PRe$·0.5(C_4H_8O)
fw	572.62	726.86
cryst system	monoclinic	triclinic
space group	$P2_1/c$	$P\bar{1}$
a, Å	8.065 (3)	17.844 (4)
b, Å	15.156 (3)	11.101 (2)
c, Å	16.896 (4)	9.704 (2)
α, deg		64.62 (2)
β, deg	95.44 (2)	75.55 (2)
γ, deg		73.20 (2)
V, Å^3	2055 (1)	1645 (1)
Z	4	2
d_{calcd}, g/cm^3	1.85	1.47
cryst dimens, mm	0.10 × 0.25 × 0.40	0.23 × 0.26 × 0.49
radiatn, Å	λ(Mo Kα) = 0.71069	λ(Mo Kα) = 0.71069
temp of collectn, °C	−160(5)	22
data collectn method	θ–2θ	θ–2θ
scan speed, deg/min^{-1}	4.0	variable, 2.0–24.0
reflctns measd	$\pm h,\pm k,+l$; 2–50°	$+h,+k,\pm l$; 3–50°
scan range	$K_{\alpha1}$−1.2 to $K_{\alpha2}$+1.2	$K_{\alpha1}$−1.0 to $K_{\alpha2}$+1.0
total bkgd time/scan time	1.0	1.0
no. of reflctns between std	97	97
total unique data	4069	5779
cutoff for obsd data	$I > 3.0\sigma(I)$	$I > 2.5\sigma(I)$
obsd data	2914	4740
abs coeff (μ), cm^{-1}	63.48	38.20
abs correctn method	none applied	ψ scans
Ψ scan reflection		262, 20 = 22.2
max/min intensity		1.12
method of refinement	block matrix least squares	block matrix least squares
no. of variables	151	423
$R = \sum(\lvert F_o - F_c\rvert)/\sum F_o$	0.044	0.040
$R_w = \sum(\lvert F_o - F_c\rvert)w^{1/2}/\sum(F_o)w^{1/2}$	0.056	0.044
weighting factor, w	$1/\sigma^2(F_o)$	$1/(\sigma^2(F_o) + 0.0045(F_o)^2)$
Δ/σ (max)	0.07	0.04

The unit cells of **1** and **2**·$(THF)_{0.5}$ were found to be monoclinic and triclinic, respectively, with the lattice parameters listed in Table I. Refinement, described in the Experimental Section, yielded the structures shown in Figure 1. All of the hydrogen atoms in **1** were located from a difference map, and the formyl hydrogen H1 was refined isotropically. In **2**·$(THF)_{0.5}$, the hydrogen atoms were

(11) (a) Parshall, G. W. *Homogeneous Catalysis*; Wiley: New York, 1980; Chapter 5. (b) Masters, C. *Homogeneous Transition-metal Catalysis*; Chapman and Hall: New York, 1981; pp 89–135, 239.
(12) (a) Berthier, G.; Serre, J. In *The Chemistry of the Carbonyl Group*; Patai, S., Ed.; Wiley-Interscience: New York, 1966; pp 3–5. (b) Iijima, T.; Tsuchiya, S. *J. Mol. Spectrosc.* **1972**, *44*, 88. (c) Iijima, T. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 3526.
(13) Casey, C. P.; Meszaros, M. W.; Neumann, S. M.; Cesa, I. G.; Haller, K. J. *Organometallics* **1985**, *4*, 143.
(14) (a) Berke, H.; Weiler, G.; Huttner, G.; Orama, O. *Chem. Ber.* **1987**, *120*, 297. (b) Berke, H.; Huttner, G.; Scheidsteger, O.; Weiler, G. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 735.
(15) Wong, W.-K.; Tam, W.; Strouse, C. E.; Gladysz, J. A. *J. Chem. Soc., Chem. Commun.* **1979**, 530.
(16) (a) Smith, D. E.; Gladysz, J. A. *Organometallics* **1985**, *4*, 1480. (b) Bodner, G. S.; Smith, D. E.; Hatton, W. G.; Heah, P. C.; Georgiou, S.; Rheingold, A. L.; Geib, S. J.; Hutchinson, J. P.; Gladysz, J. A. *J. Am. Chem. Soc.*, in press.

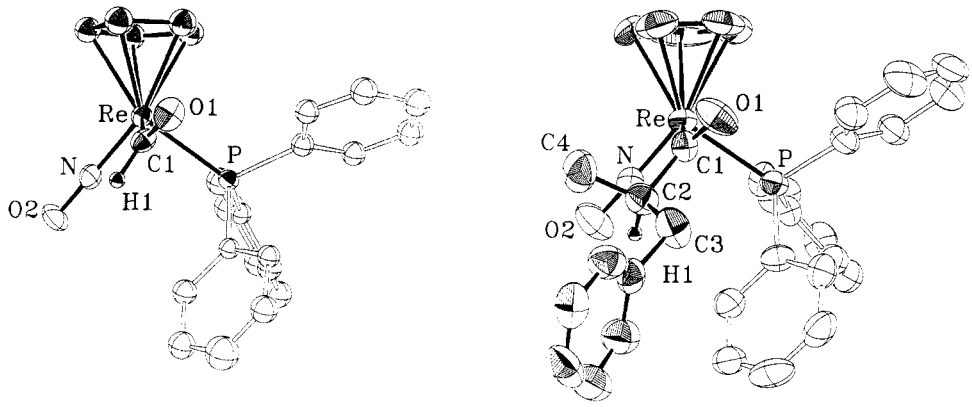


Figure 2. Molecular structures of 1 and 2·(THF)$_{0.5}$ as viewed in Newman-type projections down the C1–Re (C_α–Re) bond.

Table II. Positional Parameters of Atoms in (η^5-C_5H_5)Re(NO)(PPh_3)(CHO) (1)

atom	x	y	z
Re	0.37259 (5)	0.166648 (23)	0.108790 (21)
P	0.50533 (30)	0.27723 (15)	0.18981 (14)
O1	0.1971 (10)	0.3137 (5)	0.0203 (5)
O2	0.6822 (9)	0.1191 (5)	0.0370 (4)
N	0.5594 (11)	0.1379 (5)	0.0671 (5)
C1	0.3206 (12)	0.2668 (6)	0.0283 (6)
C21	0.1076 (14)	0.1644 (7)	0.1464 (6)
C22	0.2060 (13)	0.1197 (7)	0.2072 (6)
C23	0.2669 (13)	0.0443 (7)	0.1727 (6)
C24	0.2118 (13)	0.0407 (7)	0.0928 (6)
C25	0.1098 (14)	0.1152 (7)	0.0751 (6)
C30	0.3730 (12)	0.3413 (6)	0.2503 (5)
C31	0.4197 (12)	0.3613 (6)	0.3287 (6)
C32	0.3249 (13)	0.4188 (7)	0.3693 (6)
C33	0.1845 (13)	0.4576 (7)	0.3326 (6)
C34	0.1326 (14)	0.4353 (7)	0.2531 (6)
C35	0.2248 (12)	0.3772 (7)	0.2119 (6)
C40	0.6735 (11)	0.2387 (6)	0.2613 (5)
C41	0.8043 (13)	0.2903 (7)	0.2869 (6)
C42	0.9349 (13)	0.2606 (7)	0.3419 (6)
C43	0.9239 (14)	0.1766 (7)	0.3708 (7)
C44	0.7932 (15)	0.1228 (8)	0.3451 (7)
C45	0.6657 (14)	0.1532 (7)	0.2908 (6)
C50	0.6118 (11)	0.3630 (6)	0.1375 (5)
C51	0.7461 (13)	0.3375 (6)	0.0980 (6)
C52	0.8325 (14)	0.3984 (7)	0.0566 (6)
C53	0.7785 (13)	0.4852 (7)	0.0522 (6)
C54	0.6443 (13)	0.5097 (7)	0.0882 (6)
C55	0.5577 (12)	0.4499 (6)	0.1314 (5)
H1	0.4057 (110)	0.2797 (59)	−0.0157 (51)
H21	0.0600	0.2188	0.1563
H22	0.2477	0.1354	0.2598
H23	0.3530	−0.0054	0.1941
H24	0.2396	−0.0104	0.0424
H25	0.0525	0.1404	0.0372
H31	0.5222	0.3376	0.3527
H32	0.3620	0.4313	0.4195
H33	0.1146	0.5072	0.3630
H34	0.0431	0.4625	0.2223
H35	0.1979	0.3646	0.1563
H41	0.8229	0.3457	0.2720
H42	1.0262	0.3113	0.3611
H43	1.0164	0.1563	0.3879
H44	0.8021	0.0639	0.3752
H45	0.5750	0.1121	0.2683
H51	0.7813	0.2604	0.0968
H52	0.9203	0.3750	0.0460
H53	0.8555	0.5257	0.0236
H54	0.5938	0.5623	0.0854
H55	0.4688	0.4688	0.1563

assigned to calculated positions. Newman-type projections down the C_α–Re bonds are given in Figure 2. Positional parameters, bond distances, and bond angles are summarized in Tables II–V.

As easily seen in Figure 2, crystalline 1 and 2·(THF)$_{0.5}$ adopted Re–C_α conformations with the carbonyl oxygen anti to the nitrosyl ligand. The ON–Re–C_α–O torsion angle θ was 176° for 1 and 180° for 2·(THF)$_{0.5}$.

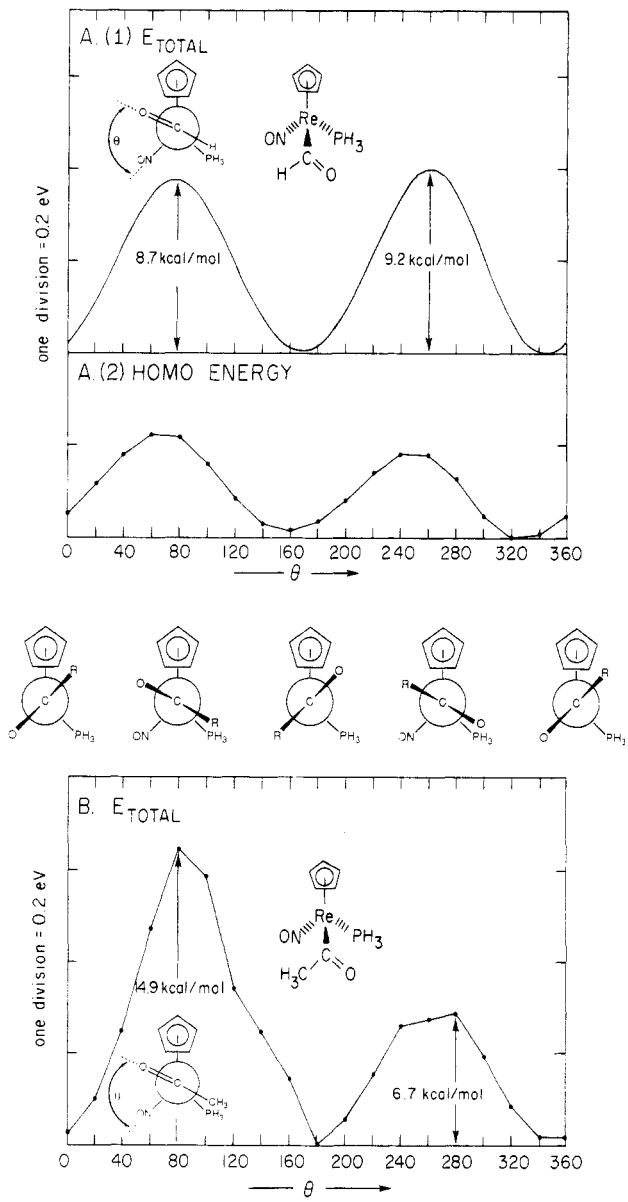


Figure 3. A. Variation in E_{total} and the HOMO energy as the formyl ligand is rotated in model complex (η^5-C_5H_5)Re(NO)(PH_3)(CHO). B. Variation in E_{total} as the acetyl ligand is rotated in model complex (η^5-C_5H_5)Re(NO)(PH_3)($COCH_3$) (calculated by the extended Hückel method with weighted H_{ij} formula; A-1, every 5°; A-2 and B, every 20°).

The structures of 1 and 2 were further analyzed by EHMO calculations on the model formyl and acetyl com-

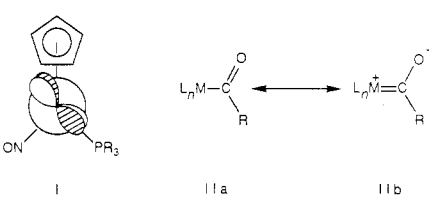
Table III. Positional Parameters of Atoms in (*SR,RS*)-(η^5-C_5H_5)Re(NO)(PPh_3)(COCH(CH_3)$CH_2C_6H_5$)•$(THF)_{0.5}$ (2•$(THF)_{0.5}$)

atom	x	y	z	atom	x	y	z
Re	0.77678 (2)	0.69634 (3)	0.63043 (3)	H4a	0.7034	1.1528	0.5021
P	0.72629 (11)	0.62324 (20)	0.48274 (22)	H4b	0.7926	1.0897	0.4696
O1	0.8451 (4)	0.8872 (6)	0.3347 (8)	H4c	0.7395	1.0087	0.6138
O2	0.6191 (4)	0.7984 (7)	0.7732 (8)	H11	0.5651	1.1828	0.2828
N	0.6820 (4)	0.7599 (7)	0.7120 (8)	H12	0.4848	1.3956	0.1979
C1	0.7858 (5)	0.8762 (8)	0.4377 (10)	H13	0.5417	1.5884	0.1033
C2	0.7228 (5)	1.0074 (8)	0.4204 (9)	H14	0.6787	1.5599	0.0806
C3	0.7226 (7)	1.0965 (9)	0.2491 (10)	H15	0.7569	1.3420	0.1384
C4	0.7410 (8)	1.0704 (11)	0.5089 (14)	H21	0.9393	0.6354	0.4830
C10	0.6693 (6)	1.2411 (9)	0.2158 (9)	H22	0.8885	0.4378	0.6463
C11	0.5884 (6)	1.2608 (12)	0.2357 (12)	H23	0.8243	0.4480	0.8962
C12	0.5403 (7)	1.3854 (14)	0.1905 (14)	H24	0.8372	0.6720	0.8888
C13	0.5743 (8)	1.4994 (12)	0.1320 (12)	H25	0.9065	0.7975	0.6225
C14	0.6551 (8)	1.4830 (11)	0.1169 (12)	H31	0.7771	0.3657	0.4477
C15	0.7009 (7)	1.3530 (10)	0.1552 (11)	H32	0.8849	0.2711	0.2997
C21	0.9117 (5)	0.6194 (11)	0.5847 (13)	H33	0.9780	0.4007	0.1384
C22	0.8842 (7)	0.5121 (11)	0.6745 (15)	H34	0.9584	0.6222	0.1035
C23	0.8489 (7)	0.5153 (16)	0.8121 (17)	H35	0.8580	0.7148	0.2557
C24	0.8557 (8)	0.6397 (17)	0.8073 (19)	H41	0.6160	0.5186	0.4093
C25	0.8945 (7)	0.7095 (11)	0.6616 (17)	H42	0.5457	0.3454	0.5490
C30	0.8055 (5)	0.5516 (9)	0.3653 (9)	H43	0.5694	0.1977	0.7974
C31	0.8147 (5)	0.4183 (9)	0.3788 (11)	H44	0.6436	0.2424	0.9249
C32	0.8788 (6)	0.3619 (11)	0.2915 (13)	H45	0.7075	0.4248	0.7960
C33	0.9328 (6)	0.4390 (13)	0.1944 (12)	H51	0.5771	0.7938	0.5273
C34	0.9229 (6)	0.5676 (14)	0.1773 (12)	H52	0.4848	0.9542	0.3741
C35	0.8617 (5)	0.6245 (10)	0.2645 (11)	H53	0.5171	1.0397	0.1053
C40	0.6674 (5)	0.4933 (7)	0.5906 (8)	H54	0.6322	0.9274	−0.0097
C41	0.6204 (5)	0.4657 (9)	0.5154 (10)	H55	0.7227	0.7533	0.1465
C42	0.5815 (6)	0.3593 (9)	0.5963 (11)	O3	0.9372 (13)	0.9037 (21)	0.8422 (24)
C43	0.5930 (6)	0.2755 (9)	0.7462 (11)	C61	0.9776 (20)	0.9829 (30)	0.7264 (37)
C44	0.6380 (6)	0.2990 (10)	0.8201 (10)	C62	0.9415 (16)	1.1238 (26)	0.7317 (30)
C45	0.6753 (6)	0.4085 (8)	0.7435 (9)	C63	0.8761 (17)	1.1101 (27)	0.8369 (31)
C50	0.6589 (5)	0.7529 (8)	0.3513 (9)	C64	0.8701 (19)	0.9782 (30)	0.9063 (36)
C51	0.5877 (5)	0.8184 (9)	0.4186 (11)	H61a	1.0322	0.9557	0.7375
C52	0.5345 (6)	0.9175 (9)	0.3274 (11)	H61b	0.9714	0.9814	0.6330
C53	0.5518 (7)	0.9642 (11)	0.1677 (13)	H62a	0.9282	1.1880	0.6334
C54	0.6213 (7)	0.9003 (10)	0.0994 (11)	H62b	0.9779	1.1529	0.7614
C55	0.6750 (6)	0.7955 (10)	0.1930 (10)	H63a	0.8792	1.1410	0.9127
H2	0.6701	0.9936	0.4587	H63b	0.8309	1.1635	0.7875
H3a	0.7754	1.1059	0.2033	H64a	0.8689	0.9465	1.0147
H3b	0.7043	1.0515	0.2036	H64b	0.8234	0.9676	0.8861

plexes (η^5-C_5H_5)Re(NO)(PH_3)(CHO) and (η^5-C_5H_5)Re(NO)(PH_3)($COCH_3$), as described in the Experimental Section.[17] Figure 3A shows the variation in E_{total} and the HOMO energy as the Re–C_α bond was rotated in formyl complex (η^5-C_5H_5)Re(NO)(PH_3)(CHO). The PH_3 ligand was held in the Re–P conformation earlier found to be optimum for ethyl complex (η^5-C_5H_5)Re(NO)(PH_3)(CH_2CH_3),[17b] and variation of the PH_3 geometry did not significantly affect E_{total}. Minima were found at θ = 170° and 345°, and maxima were at near-orthogonal formyl ligand orientations. The θ dependence of the HOMO energy accounted for ca. 60% of the θ dependence of E_{total}. The energies of the next two occupied orbitals varied less with θ and were out of phase with each other.

Figure 3B shows the variation in E_{total} as the Re–C_α bond was rotated in acetyl complex (η^5-C_5H_5)Re(NO)(PH_3)($COCH_3$). Here, E_{total} was dependent upon the PH_3 and acetyl CH_3 geometries near the energy maxima, and optimization was conducted. Minima were found at θ = 180° and 340°.

At the maxima in Figure 3, the HOMO was mainly the d orbital shown in I below, with some contribution by the C=O oxygen p lone pair perpendicular to the π bond plane. At the minima, the HOMO was highly delocalized and consisted of the bonding combination of the d orbital shown in I with the C=O π^* orbital, with some C=O oxygen lone pair.



The θ dependence of the LUMO energy was nearly perfectly out of phase with the θ dependence of E_{total} and the HOMO energy. At the E_{total} maxima (the LUMO energy minima), the LUMO consisted principally of antibonding interactions of metal d orbitals with NO π^* orbitals, with some bonding interaction of a metal d orbital and the C=O π^* orbital. At the E_{total} minima, the LUMO was strongly destabilized and was mainly an antibonding combination between metal d and NO π^* orbitals, without a C=O π^* contribution.

The effect of 10–20° angular distortions about C_α in formyl complex (η^5-C_5H_5)Re(NO)(PH_3)(CHO) was examined, with the constraint that the sum of the three C_α bond angles equal 360°. No qualitative difference in θ dependence of E_{total} was found, but there were small changes in the energies of the maxima and minima.

(17) (a) 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. (b) Georgiou, S.; Gladysz, J. A. *Tetrahedron* **1986**, *42*, 1109. (c) Schilling, B. E. R.; Hoffman, R.; Faller, J. W. *J. Am. Chem. Soc.* **1979**, *101*, 592. (d) In d^6 (η^5-C_5H_5)M(L)(L′) fragments where L is a better π acid than L′, the occupied d orbital that is in the same plane as the M–L bond (and perpendicular to the M–L′ bond) will be lower in energy than the occupied d orbital that is in the same plane as the M–L′ bond (and perpendicular to the M–L bond).[17c] Hence, the orientation of the HOMO shown in I arises from the poor π acidity of PPh_3 relative to NO.

Table IV. Bond Distances in 1 and 2•(THF)$_{0.5}$ (Å)

from	to	dist in 1	dist in 2·(THF)$_{0.5}$
Re	P	2.356 (2)	2.358 (3)
Re	N	1.777 (8)	1.758 (7)
Re	C1	2.055 (10)	2.081 (7)
Re	C21	2.287 (11)	2.303 (9)
Re	C22	2.346 (10)	2.325 (10)
Re	C23	2.347 (10)	2.320 (13)
Re	C24	2.309 (10)	2.252 (19)
Re	C25	2.279 (11)	2.245 (14)
P	C30	1.825 (10)	1.799 (9)
P	C40	1.835 (9)	1.817 (8)
P	C50	1.831 (9)	1.822 (7)
O1	C1	1.220 (12)	1.252 (10)
O2	N	1.190 (10)	1.181 (9)
C1	H	1.076 (89)	
C1	C2		1.531 (11)
C2	C3		1.524 (11)
C2	C4		1.452 (20)
C3	C10		1.549 (13)
C10	C11		1.370 (15)
C10	C15		1.347 (16)
C11	C12		1.347 (16)
C12	C13		1.394 (21)
C13	C14		1.374 (21)
C14	C15		1.375 (14)
C21	C22	1.410 (14)	1.285 (15)
C21	C25	1.418 (15)	1.409 (22)
C22	C23	1.394 (14)	1.334 (21)
C23	C24	1.382 (14)	1.398 (29)
C24	C25	1.412 (15)	1.398 (19)
C30	C31	1.376 (13)	1.388 (15)
C30	C35	1.414 (13)	1.382 (12)
C31	C32	1.383 (14)	1.402 (14)
C32	C33	1.371 (14)	1.369 (15)
C33	C34	1.409 (14)	1.325 (21)
C34	C35	1.382 (14)	1.376 (15)
C40	C41	1.351 (13)	1.404 (16)
C40	C45	1.391 (13)	1.389 (10)
C41	C42	1.410 (14)	1.377 (13)
C42	C43	1.370 (14)	1.377 (13)
C43	C44	1.370 (16)	1.338 (19)
C44	C45	1.391 (15)	1.384 (15)
C50	C51	1.381 (13)	1.420 (11)
C50	C55	1.388 (12)	1.404 (13)
C51	C52	1.384 (14)	1.367 (12)
C52	C53	1.387 (14)	1.386 (15)
C53	C54	1.343 (14)	1.398 (15)
C54	C55	1.392 (14)	1.404 (13)
O3	C61		1.290 (35)
O3	C64		1.411 (37)
C61	C62		1.523 (44)
C62	C63		1.339 (36)
C63	C64		1.346 (42)

Discussion

Structure and Bonding about Rhenium. All of the metal–ligand bond distances in 1 and 2·(THF)$_{0.5}$ are very similar (Table IV). Both 1 and 2·(THF)$_{0.5}$ exhibit the ca. 90° N–Re–C1, C1–Re–P, and P–Re–N bond angles (C1 = C_α) expected for octahedral complexes (Table V). Figures 1 and 2 show that the orientations of the cyclopentadienyl and PPh_3 ligands in 1 and 2·(THF)$_{0.5}$ are remarkably alike. The acute C1–Re–C25 bond angles (87.8 (4)°, 84.4 (4)°) indicate that the C25 cyclopentadienyl carbons extend into the C_α side of the N–Re–P plane. The C1–Re–C21 bond angles (93.3 (4)°, 89.7 (3)°) show that the C21 cyclopentadienyl carbons are very close to the N–Re–P plane.

Previous EHMO calculations have established that the HOMO of the $(\eta^5\text{-}C_5H_5)Re(NO)(PR_3)^+$ fragment is the d orbital shown in I.[17] This result is supported experimentally by the X-ray crystal structures of benzylidene complex *ac*-$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(=CHC_6H_5)]^+PF_6^-$ and π-formaldehyde complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^2\text{-}H_2C{=}O)]^+PF_6^-$.[17a,18] The unsaturated ligands in these and related[19] complexes adopt conformations that maximize overlap of their acceptor orbitals with the d orbital shown in I. However, in formyl and acyl complexes such as 1 and 2·(THF)$_{0.5}$, the C=O π and π^* orbitals are both of appropriate symmetry to mix with the d orbital shown in I. Importantly, our calculations ($PR_3 = PH_3$) show that the d orbital is closer in energy to the $HC{=}O^-$ fragment π^* orbital ($\Delta E \simeq 2.4$ eV) than to the $HC{=}O^-$ fragment π orbital ($\Delta E \simeq 3.3$ eV). Thus, the attractive interaction between the occupied d orbital and unoccupied π^* acceptor orbital is expected to dominate.[20]

Figure 2 clearly shows that the formyl and acyl ligands in 1 and 2·(THF)$_{0.5}$ adopt one of two Re–C_α conformations that maximize overlap of their C=O π^* acceptor orbitals with the d orbital shown in I. The ligands also adopt conformations that minimize the HOMO energies, as predicted by Walsh's rule.[21] Thus, resonance form IIb should significantly contribute to the structures of these molecules. Accordingly, we have previously noted that $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(COR)$ complexes exhibit IR $\nu_{C=O}$ of 1515–1560 cm^{-1}.[22] These frequencies are distinctly lower than the $\nu_{C=O}$ of tertiary amides (R'_2NCOR; 1630–1680 cm^{-1}), where the corresponding resonance interaction involves a basic nitrogen atom.[23]

As expected from the above analysis, the Re–C_α bond lengths in 1 and 2·(THF)$_{0.5}$ (2.055 (10), 2.081 (7) Å) are significantly shorter than those found in rhenium alkyl complexes such as (−)-(*R*)-$(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2C_6H_5)$ (2.203 (8) Å)[24] and (*SS,RR*)-$(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH(CH_2C_6H_5)C_6H_5)$ (2.215 (4) Å).[17a] The Re–C_α bonds are, however, longer than the Re=C_α double bond in benzylidene complex *ac*-$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(=CHC_6H_5)]^+PF_6^-$ (1.949 (6) Å).[17a]

Fenske has also performed, using a higher level of theory, MO calculations on $(\eta^5\text{-}C_5H_5)Re(NO)(PH_3)(CHO)$ in a conformation with θ near 180°.[25] Our data on Re–C_α bonding and key HOMO and LUMO contributions are in qualitative agreement with his.

Structure, Bonding, and Orientation of the Formyl and Acyl Ligands. The formyl and acyl ligands in 1 and 2·(THF)$_{0.5}$ exhibit very similar geometries. The C1–O1 (C_α–O) bond lengths (1.220 (12), 1.252 (10) Å) are not significantly different and are close to the carbonyl bond lengths of formamide and acetamide (1.255 (13), 1.260 (13) Å; X-ray data).[26] The Re–C1–O1 bond angle in 1 (128.1 (8)°) is slightly greater than that in 2·(THF)$_{0.5}$ (122.7 (6)°), perhaps because of the smaller hydrogen substituent on C_α. Similarly, the C—C=O and N—C=O bond angles in acetaldehyde and formamide (124.2 (5)°, 125.0 (4)°) are slightly greater than those in methyl-substituted homologues acetone and acetamide (122.0 (2)°, 122.0 (5)°).[12b,c,26] The Re–C1–H1 angle in 1 is, as expected from X-ray data, not very accurate.

(18) Buhro, W. E.; Georgiou, S.; Fernández, J. M.; Patton, A. T.; Strouse, C. E.; Gladysz, J. A. *Organometallics* **1986**, *6*, 956.
(19) (a) Patton, A. T.; Strouse, C. E.; Knobler, C. B.; Gladysz, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 5804. (b) Fernández, J. M.; Emerson, K.; Larsen, R. H.; Gladysz, J. A. *J. Am. Chem. Soc.* **1986**, *108*, 8268.
(20) These points are discussed in additional detail in reference 16b. See also Kostić, N. M.; Fenske, R. F. *Organometallics* **1982**, *1*, 974.
(21) Albright, T. A.; Burdett, J. K.; Whangbo, M.-H. *Orbital Interactions in Chemistry*; Wiley: New York, 1985; p 94.
(22) Buhro, W. E.; Wong, A.; Merrifield, J. H.; Lin, G.-Y.; Constable, A. G.; Gladysz, J. A. *Organometallics* **1983**, *2*, 1852.
(23) Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectrometric Identification of Organic Compounds*, 4th ed.; Wiley: New York, 1981; p 126.
(24) Merrifield, J. H.; Strouse, C. E.; Gladysz, J. A. *Organometallics* **1982**, *1*, 1204.
(25) Fenske, R. F.; Milletti, M. C.; Arndt, M. *Organometallics* **1986**, *5*, 2316.
(26) Kitano, M.; Kuchitsu, K. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 67.

Table V. Bond Angles in 1 and 2•(THF)$_{0.5}$ (deg)

from	thru	to	angle in 1	angle in 2·(THF)$_{0.5}$	from	thru	to	angle in 1	angle in 2·(THF)$_{0.5}$
P	Re	N	92.8 (3)	93.4 (3)	C11	C12	C13		118.1 (12)
P	Re	C1	85.0 (3)	88.3 (3)	C12	C13	C14		120.0 (11)
P	Re	C21	103.5 (3)	103.5 (4)	C13	C14	C15		118.5 (12)
P	Re	C22	93.6 (3)	92.8 (4)	C14	C15	C16		122.5 (11)
P	Re	C23	117.4 (3)	112.1 (5)	Re	C21	C22	74.6 (6)	74.8 (6)
P	Re	C24	151.1 (3)	147.2 (5)	Re	C21	C25	71.6 (6)	69.7 (6)
P	Re	C25	138.5 (3)	138.6 (4)	C22	C21	C25	108.4 (9)	109.0 (11)
N	Re	C1	92.7 (4)	95.6 (3)	Re	C22	C21	70.0 (6)	72.9 (6)
N	Re	C21	163.0 (4)	162.5 (5)	Re	C22	C23	72.8 (6)	72.5 (7)
N	Re	C22	140.4 (4)	143.9 (3)	C21	C22	C23	106.6 (9)	113.1 (15)
N	Re	C23	110.3 (4)	112.9 (4)	Re	C23	C22	72.7 (6)	73.5 (7)
N	Re	C24	103.8 (4)	104.8 (5)	Re	C23	C24	71.2 (6)	69.6 (9)
N	Re	C25	128.4 (4)	127.8 (5)	Re	C24	C23	74.2 (6)	74.9 (11)
C1	Re	C21	93.3 (4)	89.7 (3)	Re	C24	C25	70.9 (6)	71.6 (10)
C1	Re	C22	126.8 (4)	120.1 (3)	C22	C23	C24	110.3 (9)	105.3 (12)
C1	Re	C23	145.9 (4)	142.9 (3)	C23	C24	C25	107.6 (9)	108.5 (16)
C1	Re	C24	117.1 (4)	116.1 (5)	Re	C25	C21	72.2 (6)	74.2 (8)
C1	Re	C25	87.8 (4)	84.4 (4)	Re	C25	C24	73.2 (6)	63.2 (5)
C21	Re	C22	35.4 (4)	32.2 (4)	C21	C25	C24	107.1 (9)	104.1 (13)
C21	Re	C23	58.0 (4)	56.4 (4)	P	C30	C31	122.4 (7)	120.9 (6)
C21	Re	C24	59.4 (4)	58.1 (5)	P	C30	C35	117.5 (7)	121.3 (8)
C21	Re	C25	36.2 (4)	36.1 (5)	C31	C30	C35	119.9 (9)	117.7 (8)
C22	Re	C23	34.6 (4)	33.4 (5)	C30	C31	C32	120.2 (9)	120.3 (8)
C22	Re	C24	58.6 (4)	56.6 (6)	C31	C32	C33	121.2 (10)	119.3 (12)
C22	Re	C25	59.4 (4)	54.4 (7)	C32	C33	C34	119.1 (10)	120.6 (10)
C23	Re	C24	34.5 (4)	35.6 (7)	C33	C34	C35	120.5 (10)	121.3 (10)
C23	Re	C25	58.3 (4)	59.6 (5)	C30	C35	C34	119.1 (9)	120.7 (11)
C24	Re	C25	35.8 (4)	36.2 (5)	P	C40	C41	121.7 (7)	120.2 (5)
Re	P	C30	116.5 (4)	110.8 (4)	P	C40	C45	118.0 (7)	120.9 (8)
Re	P	C40	114.7 (4)	116.2 (3)	C41	C40	C45	119.0 (9)	118.4 (8)
Re	P	C50	115.6 (4)	116.5 (3)	C40	C41	C42	122.6 (10)	119.3 (8)
C30	P	C40	103.3 (4)	105.3 (5)	C41	C42	C43	117.5 (10)	120.2 (11)
C30	P	C50	102.6 (4)	105.9 (4)	C42	C43	C44	121.0 (11)	121.6 (10)
C40	P	C50	100.8 (4)	101.0 (4)	C43	C44	C45	120.7 (11)	119.4 (8)
Re	N	O2	178.0 (8)	177.0 (6)	C40	C45	C44	119.3 (10)	121.0 (11)
Re	C1	O1	128.1 (8)	122.7 (6)	P	C50	C51	117.4 (7)	116.8 (6)
Re	C1	H1	119.2 (48)		P	C50	C55	123.4 (7)	124.2 (6)
Re	C1	C2		121.4 (5)	C51	C50	C55	119.0 (9)	118.9 (7)
O2	C1	H1	112.7		C50	C51	C52	120.9 (9)	120.2 (9)
O2	C1	C2		115.6 (6)	C51	C52	C53	119.3 (10)	120.9 (9)
C1	C2	C3		108.9 (7)	C52	C53	C54	120.1 (10)	119.4 (9)
C1	C2	C4		106.8 (9)	C53	C54	C55	121.6 (10)	119.6 (10)
C2	C3	C10		114.1 (8)	C50	C55	C54	119.2 (9)	120.7 (9)
C3	C2	C4		114.3 (9)	C61	O3	C64		111.9 (23)
C3	C10	C11		121.2 (10)	O3	C61	C62		103.9 (25)
C3	C10	C15		121.2 (9)	C61	C62	C63		106.0 (25)
C11	C10	C15		117.4 (9)	C62	C63	C64		110.3 (26)
C10	C11	C12		123.2 (12)	O3	C64	C63		106.8 (24)

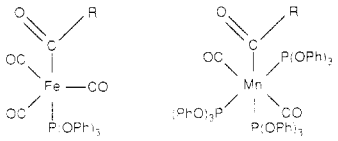
The EHMO calculations predict the two Re–C$_\alpha$ conformational minima of formyl complex (η^5-C$_5$H$_5$)Re(NO)(PH$_3$)(CHO) to be of nearly equal energy (Figure 3A). The two Re–C$_\alpha$ minima of acetyl complex (η^5-C$_5$H$_5$)Re(NO)(PH$_3$)(COCH$_3$) are slightly more separated, with the rotamer with θ = 180° more stable by 0.8 kcal/mol (Figure 3B). It is not considered advisible to interpret small energy differences obtained by EHMO calculations. Our bias, however, is that acyl complex Re–C$_\alpha$ rotamers with θ near 180° should be favored on steric grounds. The NO ligand is smaller than both the PR$_3$ and cyclopentadienyl ligands, and it seems that the larger C$_\alpha$ substituent (alkyl) should prefer to be syn to the NO ligand and the smaller C$_\alpha$ substituent (=O) should therefore be anti to the NO ligand.[27] However, regardless of the prediction of any theoretical model, it is important to keep in mind that the X-ray crystal structures of 1 and 2·(THF)$_{0.5}$ do not in themselves establish the thermodynamically preferred Re–C$_\alpha$ conformations in solution.[28a]

Structural and Theoretical Studies on Related Complexes. Several studies by other researchers are particularly relevant to our results. First, Casey and coworkers have determined the X-ray crystal structures of formyl complex (CH$_3$CH$_2$)$_4$N$^+$ *trans*-[((PhO)$_3$P)Fe(CO)$_3$(CHO)]$^-$ (3) and acetyl complex (CH$_3$CH$_2$)$_4$N$^+$ *trans*-[((PhO)$_3$P)Fe(CO)$_3$(COCH$_3$)]$^-$ (4).[13] These complexes (and the others that follow) exhibit higher IR $\nu_{C=O}$ (1580–1588 cm^{-1}) than 1 and 2·(THF)$_{0.5}$, suggesting slightly less contribution from resonance form IIb. In contrast to our findings with 1 and 2·(THF)$_{0.5}$, the C$_\alpha$–O bond length of formyl complex 3 (1.166 (4) Å) is significantly shorter than that of acetyl complex 4 (1.226 (5) Å). Also, 3 and 4 exhibit somewhat different Fe–C$_\alpha$ conformations, with OC–Fe–C$_\alpha$–O torsion angles that differ by 39°.[28b] As with 1 and

(27) The Re–P bond is perpendicular to the C$_\beta$–C$_\alpha$–O plane of 2·(THF)$_{0.5}$ in Re–C$_\alpha$ conformations with θ = 0° *and* 180°. Hence, if the Re–PPh$_3$ rotamers are averaged, the PPh$_3$ ligand should exert an equal steric effect upon the acyl ligand in each Re–C$_\alpha$ conformation, leaving the relative sizes of the NO and cyclopentadienyl ligands as a key conformation-determining factor. We noted above that C21 and C25 are in (or on the C$_\alpha$ side of) the N–Re–P plane, so the cyclopentadienyl hydrogens should exert a significant steric effect; see Figure 6 in ref 16b.

(28) (a) **Note Added in Proof**: Irradiation of the η^5-C$_5$H$_5$ ^{1}H NMR resonance of 1 gives a 2.1% difference NOE enhancement of the formyl proton. On the basis of data described elsewhere,[16b] this suggests the presence of some Re–C$_\alpha$ conformer with θ near 0° in solution. (b) This value is calculated from the difference in C(5)–Fe–C(1)–O(1) torsion angles, where C(5) is the crystallographically unique carbonyl carbon of the (L)(CO)$_3$Fe fragment; see Figures 1–3, ref 13.

2·$(THF)_{0.5}$, the M–C_α–O bond angle is greater in formyl complex **3** (133.0 (3) Å) than in acyl complex **4** (125.7 (3) Å). Casey suggested that the larger angle may be a reflection of the hydride donor capability of formyl complexes—a process that gives a linear carbonyl ligand.[13] Casey has also reported the X-ray crystal structure of the related triarylphosphite-substituted formyl complex $(CH_3CH_2)_4N^+$ *trans*-$[((3,5\text{-}C_6(CH_3)_2H_3O)_3P)Fe(CO)_3(CHO)]^-$ and finds a structure essentially identical to that of **3**.[29]

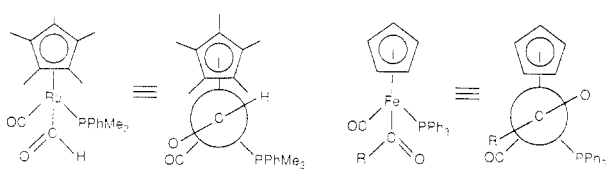


3. R = H 5. R = H

4. R = CH_3 6. R = CH_3

Berke and co-workers have determined the X-ray crystal structures of formyl complex $((PhO)_3P)_3Mn(CO)_2(CHO)$ (**5**) and acetyl complex $((PhO)_3P)_3Mn(CO)_2(COCH_3)$ (**6**).[14] The C_α–O bond lengths are not significantly different (121 (1), 120.3 (9) Å), but the M–C_α–O angle is again slightly greater in formyl complex **5** (126.5 (5)°, 122.6 (5)°). Complexes **5** and **6** exhibit slightly different L–Mn–C_α bond angles and Mn–C_α conformations. Berke has proposed a EHMO rationale for these structural dissimilarities that derives from differences in spacial properties of the $HC{=}O^-$ and $H_3CC{=}O^-$ fragment orbitals.[14a]

Nelson has recently reported the X-ray crystal structure of pentamethylcyclopentadienyl ruthenium formyl complex $(\eta^5\text{-}C_5Me_5)Ru(CO)(PPhMe_2)(CHO)$ (**7**).[30] This compound has a very short C_α–O bond (1.106 (5) Å) and a large Ru–C_α–O bond angle (140.0 (3)°). It is also expected to have a metal fragment HOMO similar to the d orbital shown in I.[17c] However, the M–C_α conformation of the formyl ligand is *opposite* to that of **1**, with the OC–Ru–C_α–O torsion angle near 0°, as shown in III. Provided that both of these compounds crystallize in the more stable M–C_α conformation, a plausible rationale would be that the bulkier pentamethylcyclopentadienyl ligand causes the Ru–C_α conformation with the larger C_α substituent (=O) syn to the small CO ligand to be favored.



7 III 8 IV

To date, the crystal structures of three other formyl complexes have been described in the literature. Wayland has reported the structure of (OEP)Rh(CHO) (OEP = octaethylporphyrin), which has a C_α–O bond length of 1.175 (5) Å and a Rh–C_α–O bond angle of 129.6 (5) Å.[8b] Cole-Hamilton has determined the structures of *trans*-$[(Ph_2PCH_2CH_2PPh_2)_2Os(CO)(CHO)]^+SbF_6^-\cdot CH_2Cl_2$ and deuterioformyl *trans*-$[(Ph_2PCH_2CH_2PPh_2)_2Ru(CO)(CDO)]^+SbF_6^-\cdot CH_2Cl_2$, which have C_α–O bond lengths of 1.181 (11) and 1.19 (1) Å and M–C_α–O bond angles of 130.7 (27)° and 133(3)°, respectively.[31] These data show there to be a great deal of structural similarity, particularly in the large M–C_α–O bond angles (126–140°), between diverse types of formyl complexes.

The X-ray crystal structures of several iron acyl complex of the formula $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(COR)$ (**8**) have been reported, primarily by Davies and coworkers.[32] The metal fragment is expected to have a HOMO analogous to the d orbital shown in I above.[17c] Seeman and Davies have noted that Fe–C_α conformations with the OC–Fe–C_α–O torsion angle (θ) near 180°, as shown in IV, are found in every crystal structure.[32] They performed EHMO calculations on the model acetyl complex $(\eta^5\text{-}C_5H_5)Fe(CO)(PPhH_2)(COCH_3)$ and obtained results similar to those in Figure 3. Distributed multiple analysis of an ab initio SCF MO calculation on the simpler model complex $(\eta^5\text{-}C_5H_5)Fe(CO)(PH_3)(COCH_3)$ predicted that Fe–C_α conformations with $\theta = 0°$ should be more stable than those with $\theta = 180°$, in contrast with the crystal structures. Additional analysis of the X-ray data showed that in every compound an ortho hydrogen of one PPh_3 phenyl ring pointed in the direction of the acyl oxygen, with an interatomic distance in one case of 1.6 Å. In Fe–C_α conformations with θ near 0°, this ortho hydrogen would be close to a much larger alkyl group. Hence, Seeman and Davies ascribed the preference for Fe–C_α conformations with θ near 180° to steric effects.[32]

As is evident in Figures 1 and 2, steric interactions of C_α alkyl substituents with the C35–H bond could occur in our complexes. We believe that this, and/or an analogous interaction with cyclopentadienyl ligand protons,[27] may be one of the main Re–C_α conformation-determining factors for **2**·$(THF)_{0.5}$. However, the formyl ligand in **1** would seem to prefer to orient its smaller C_α substituent (H) in the direction of C35, rather than its larger C_α substituent (=O) as observed. Hence, this cannot (provided the crystal structure of **1** reflects the thermodynamically favored Re–C_α conformation)[28a] be an important conformation-determining factor for **1**. Thus, other factors contributing to the Re–C_α conformation observed for **1** likely remain to be recognized.

Conclusion. Formyl complex **1** and acyl complex **2**·$(THF)_{0.5}$ exhibit very similar crystal structures. The formyl and acyl ligands show, except for a slightly greater Re–C_α–O bond angle in the former, only very minor geometric differences, and possess one of the two Re–C_α conformations that are predicted by simple frontier MO theory.[33] The steric effects of a PPh_3 phenyl ring or cyclopentadienyl ligand may play an important role in determining which of the two electronically preferred Re–C_α conformations is favored for **2**·$(THF)_{0.5}$. However, the key factors that determine the analogous conformational choice in **1** are not presently recognized.

Experimental Section

X-ray Crystal Structure of $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CHO)$ (1). Honey yellow crystals of **1** were grown as previously described.[5a] A crystal was mounted on a glass fiber and immediately

(29) Casey, C. P.; McAlister, D. R.; Calabrese, J. C.; Neumann, S. M.; Andrews, M. A.; Meszaros, M. W.; Haller, K. J. *Cryst. Struct. Commun.* **1982**, *11*, 1015.

(30) Nelson, G. O.; Sumner, C. E. *Organometallics* **1986**, *5*, 1983.

(31) (a) Smith, G.; Cole-Hamilton, D. J.; Thornton-Pett, M.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1983**, 2501. (b) Smith, G.; Cole-Hamilton, D. J.; Thornton-Pett, M.; Hursthouse, M. B. *Ibid.* **1985**, 387.

(32) (a) Davies, S. G.; Seeman, J. I.; Williams, I. H. *Tetrahedron Lett.* **1986**, *27*, 619. (b) Brown, S. L.; Davies, S. G.; Foster, D. F.; Seeman, J. I.; Warner, P. *Ibid* **1986**, *27*, 623.

(33) The conformations of many molecules arise from combinations of steric and electronic effects that are difficult to partition. However, we believe that the H–C_α–O and C_β–C_α–O planes defined by the formyl and acyl ligands in **1** and **2**·$(THF)_{0.5}$ (which are the same for both $\theta = 0°$ and 180°) are due principally to the Re–C_α frontier orbital interaction, as opposed to a steric effect of a PPh_3 phenyl ring (e.g., C50–C55). The case may be different for related iron complexes.[32a]

transferred to a Syntex P$\bar{1}$ automatic diffractometer that was equipped with a nitrogen-stream low-temperature device set at −160 ± 5 °C. The general procedure used has been described.[34] Lattice parameters (Table I) were determined from a least-squares fit of 15 automatically centered reflections. Details of data collection are given in Table I. The intensities of the three standard reflections decreased by 35–52% in a nearly linear manner over the period of data collection. Data were corrected for Lorentz and polarization effects and for a 41% loss of intensity over time. Of 3807 unique reflections, 2914 with $I > 3\sigma(I)$ were used. The position of the rhenium atom was determined from a three dimensional Patterson map. Several cycles of least-squares refinement, followed by a difference-Fourier synthesis, yielded all non-hydrogen atoms.

The atomic parameters were refined via a block-diagonal least-squares matrix. All least-squares refinements computed R and R_w according to the formulae in Table I, where F_o and F_c are the observed and calculated structure factors, respectively. The parameter minimized in all least-squares refinements was $\sum w_i|F_o - F_c|^2$.

The atoms Re, C1, O1, N, O2, and P were refined with anisotropic temperature factors. All other non-hydrogen atoms were refined with isotropic thermal parameters. All hydrogens were located from a difference Fourier map. The formyl hydrogen H1 was refined isotropically. All other hydrogen atoms were held at positions indicated from the map, and their isotropic thermal parameters were fixed at 2.0 Å^2.

X-ray Crystal Structure of (*SR,RS*)-(η^5-C_5H_5)Re(NO)(PPh$_3$)(COCH(CH$_3$)CH$_2$C$_6$H$_5$)·(THF)$_{0.5}$ (2·(THF)$_{0.5}$). A THF solution of **2**[16] was layered with hexanes. Yellow prisms formed, which were shown to be the solvate **2**·(THF)$_{0.5}$ by ^{1}H NMR and microanalysis (Galbraith). Calcd for $C_{33}H_{31}NO_2PRe\cdot(C_4H_8O)_{0.5}$: C, 57.84; H, 4.85. Found: C, 58.03; H, 4.93. A crystal was mounted on a glass fiber and coated with a thin film of epoxy. The crystal was transferred to a Syntex P$\bar{1}$ automatic diffractometer for data collection as described in Table I. Lattice parameters (Table I) were determined via a least-squares fitting of the setting angles of 15 centered reflections with 2θ between 20° and 25°. The data were corrected for Lorentz and polarization effects in the usual manner. The general techniques employed have been described.[35] Of 5779 unique reflections with $2\theta < 50°$ collected, 4740 with I $\geq 2.5\sigma(E)$ were used. The position of the rhenium atom was located from a three-dimensional Patterson map. Several least squares refinements, followed by a difference-Fourier synthesis, yielded all non-hydrogen atoms. Two additional reflections (182; F_o = 14.03, F_c = 62.98, and 384; F_o = 13.70, F_c = 63.04) were discarded because of excessive deviation between observed and calculated structure factors. Absorption corrections based upon a series of ψ scans were applied, and all non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were assigned carbon–hydrogen distances of 0.95 Å and held in their calculated positions. Density measurements (1.53 g/cm^3) suggested unit occupancy for the THF solvate. Refinement as such led to excessive thermal parameters and poor definition of the solvate. Fixing the isothermal parameter at 0.1 Å^2 and refining the occupancy gave an occupancy value of 0.5, consistent with the above analyses. Thus, the THF solvate was assigned half-occupancy and refined with isotropic thermal factors to an acceptable solution. Both R and R_w were computed as described above. Calculations were performed on the University of Utah, College of Science, DEC 20 computer with a locally modified version of SHELX-76.[36] The analytical scattering factors for neutral atoms were corrected for the real and imaginary components of anomalous dispersion.[37]

Calculations. Extended Hückel calculations[38] were conducted with weighted H_{ij} formula. The rhenium, phosphorus, and acetyl methyl carbon were assigned idealized octahedral, tetrahedral, and tetrahedral geometries, respectively. The formyl and acetyl carbonyl carbons were assigned idealized trigonal-planar geometries. The Re-C$_\alpha$ bonds were assigned lengths of 2.10 Å, the C=O bonds were assigned lengths of 1.22 Å, the formyl C–H bond was assigned a length of 1.09 Å, and the acetyl C$_\alpha$–C$_\beta$ bond was assigned a length of 1.54 Å. Other bond lengths, and the parameters utilized, were as reported earlier.[17a,b,18]

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Registry No. 1, 70083-74-8; 2, 97210-78-1; 2·(THF)$_{0.5}$, 97275-73-5; (η^5-C_5H_5)Re(NO)(PH$_3$)(CHO), 109532-07-2; (η^5-C_5H_5)Re(NO)(PH3)(COCH3), 109532-08-3.

Supplementary Material Available: Tables of thermal parameters for 1 and 2·(THF)$_{0.5}$ (3 pages); listings of structure factors for 1 and 2·(THF)$_{0.5}$ (31 pages). Ordering information is given on any current masthead page.

(34) Strouse, J.; Layten, S. W.; Strouse, C. E. *J. Am. Chem. Soc.* **1978**, *99*, 562.
(35) Churchill, M. R.; Lashewcyz, R. A.; Rotella, F. J. *Inorg. Chem.* **1977**, *16*, 265.
(36) Sheldrick, G. M. SHELX-76 program for crystal structure determinations. University of Cambridge, England, 1976.
(37) Cromer, D. T.; Waber, J. T. In *International Tables for X-ray Crystallography*; Ibers, J. A., Hamilton, W. C., Eds.; Kynoch: Birmingham, England, 1974; Vol. IV, pp 99–101, 149–150.
(38) (a) Hoffmann, R. *J. Chem. Phys.* **1963**, *39*, 1397. (b) Hoffmann, R.; Lipscomb, W. N. *Ibid.* **1962**, *36*, 2179, 3489; **1962**, *37*, 2872.