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(25) The slow decay of the quinoxalinium radical in solution complicates kinetic study of the reactions of this radical with the more sluggish oxidants. In attempted measurements, with [QH·] at the 0.004 M level and $[Co(NH_3)_5(py)^{3+}]$ at the 0.04 M level, it was found that less than 5% of the radical was oxidized in 30 min, indicating a bimolecular redox specific rate less than 0.03 $M^{-1}\ s^{-1}$ (25 °C, 1.0 M $HClO_4$).

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Reactions of Coordinated Molecules. 18. Complexes of the Triacylmetalate Dianions

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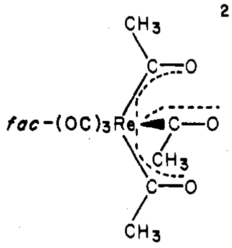
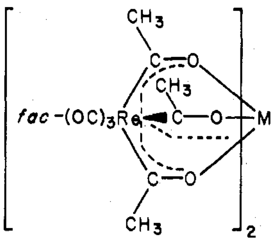
Triacylmetalate dianions of the type $[fac\text{-}(OC)_3Re(CH_3CO)_2(RCO)]^{2-}$, where R is methyl, isopropyl, benzyl, or the bridging ligands $(CH_2)_n$ where n is 5 or 6, are prepared from the corresponding neutral acylpentacarbonylrhenium complexes and 2 equiv of methyllithium. The formation of these anions is followed by IR, and the triacetyl dianion is isolated as the PPN salt. These dianions form bis-chelate complexes with Al(III), Ga(III), Hf(IV), and Zr(IV) metal ions. The aluminum and gallium complexes are anionic while the hafnium and zirconium complexes are neutral. The ligands act as tridentate chelates possessing idealized C_{3v} symmetry. This coordination geometry is confirmed by the observation of geometrical isomers for those complexes having unsymmetrically substituted ligands.

In a previous communication we reported the stoichiometric preparation of the triacetyltricarbonylrhenate dianion $fac\text{-}(OC)_3Re(CH_3CO)_3^{2-}$, **1**, and its coordination to Al(III) and Hf(IV) metal ions.[1] This dianion is a formal, metalla analogue of the triacetylmethanide anion, and it coordinates to metal ions presumably as a symmetrical tridentate chelating ligand as shown in **2**. To our knowledge dianions like **1** are the only known trioxygen ligands which coordinate as vicinal, bifurcated chelates.[2,3] These dianionic ligands also possess a formally π-delocalized electronic system.



1



2

We wish to report a general preparative procedure for the synthesis of these metalla ligands and their coordination complexes and to confirm the structure of the metal complexes **2** by demonstrating the existence of the expected geometrical isomerism when one of the alkyl substituents of each ligand is not a methyl group.[4]

The metal complexes **2** represent discrete molecules containing three metal atoms which are connected via unsaturated carbon–oxygen linkages. The central coordinating metal atom may be either a transition-metal or a main-group metal ion. These complexes are related to the metalla-β-diketonate complexes,[4] and they represent another type of polymetallic molecule which lacks direct metal–metal bonding. Such species may be relevant in catalytic processes particularly when multifunctional group activation and protection is required simultaneously.

Experimental Section

All reactions and other manipulations were performed under dry, prepurified nitrogen at 25 °C unless otherwise stated. Diethyl ether, tetrahydrofuran, benzene, toluene, hexane, and pentane were dried over Na/K alloy, and methylene chloride was dried over phosphorus pentoxide under a nitrogen atmosphere. Other solvents were dried over 4A molecular sieves and were purged with nitrogen before use. Decacarbonyldirhenium was purchased from Pressure Chemical Co. (Pittsburgh, PA). Anhydrous gallium trichloride, hafnium tetrachloride, and zirconium tetrachloride were purchased from Ventron Corp. and were handled under an argon atmosphere in a glovebag.

Infrared spectra were recorded on a Perkin-Elmer 727 spectrometer as methylene chloride solutions in 0.10-mm sodium chloride cavity cells with the solvent as a reference and a polystyrene film as a calibration standard. Band frequencies are reported in cm^{-1}. Proton NMR spectra were obtained on a JEOL MH-100 NMR spectrometer with Me_4Si as an internal reference.

Microanalyses were performed by Galbraith Laboratories, Inc. (Knoxville, TN).

$CH_3C(O)Re(CO)_5$,[5] **3**, $(CH_3)_2CHC(O)Re(CO)_5$,[4] **4**, and $C_6H_5CH_2C(O)Re(CO)_5$,[6] **5**, were prepared by slight modifications of known procedures with the pentacarbonylrhenate anion and the appropriate acyl chloride.

General Preparation of $[(OC)_5ReC(O)CH_2]_2(CH_2)_n$ Where n Is 4 or 5. To a stirred solution of $NaRe(CO)_5$ in 50 mL of THF at −78 °C was added dropwise 0.5 molar equiv of the appropriate diacid dichloride. After being stirred at −78 °C for 30 min, the reaction

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was allowed to warm slowly to 0 °C and stirred for an additional 30 min. The solvent was removed under reduced pressure affording an orange residue. The residue was extracted with methylene chloride and filtered, and the solvent was removed from the filtrate under reduced pressure. The specific data for each complex are provided below.

$[(OC)_5ReC(O)CH_2]_2(CH_2)_4$, 6. From 4.24 g (9.30 mmol) of $NaRe(CO)_5$ and 0.84 mL (4.65 mmol) of suberyl dichloride followed by crystallization from a methylene chloride–hexane (1:1) mixture, 2.20 g (62%) of the product was obtained as a pale yellow solid, dec pt 121–126 °C. IR (CH_2Cl_2): ν(CO) 2130 (w), 2045 (w, sh), 2030 (vs), 1995 (m, sh); ν(acyl) 1607 (m) cm^{-1}. ^{1}H NMR ($CDCl_3$): τ 8.72 (m, 8, CH_2), 7.30 (t, 4, $C(O)CH_2$). Anal. Calcd for $C_{18}H_{12}O_{12}Re_2$: C, 27.27; H, 1.53. Found: C, 27.50; H, 1.66.

$[(OC)_5ReC(O)CH_2]_2(CH_2)_5$, 7. From 1.38 g (3.10 mmol) of $NaRe(CO)_5$ and 0.24 mL (1.54 mmol) of azelayl dichloride followed by crystallization from diethyl ether, 0.83 g (67%) of the product was obtained as a light yellow solid, dec pt 99–104 °C. IR (CH_2Cl_2): ν(CO) 2130 (w), 2050 (w, sh), 2030 (vs), 1995 (m, sh); ν(acyl) 1608 (m) cm^{-1}. ^{1}H NMR ($CDCl_3$): τ 8.74 (m, 10, CH_2), 7.29 (t, 4, $C(O)CH_2$). Anal. Calcd for $C_{19}H_{14}O_{12}Re_2$: C, 28.29; H, 1.75. Found: C, 28.16; H, 1.83.

Preparation of (PPN)$_2$[*fac*-$(OC)_3Re(CH_3CO)_3$]·$^3/_4$THF, 8. To a solution of 0.14 g (0.38 mmol) of acetylpentacarbonylrhenium, **3**, in 40 mL of THF was added 0.48 mL (0.76 mmol) of methyllithium (1.6 M). The reaction was stirred for 1 h at 0 °C and then was treated with a CH_2Cl_2 solution of 0.44 g (0.70 mmol) of bis(triphenylphosphine)iminium (PPN) chloride. Immediately a white precipitate formed, and the reaction changed gradually to yellow. The reaction was stirred for an additional 30 min at 25 °C, and then the solvent was removed under reduced pressure. The reaction residue was extracted with methylene chloride and filtered, and the solvent was removed from the filtrate under reduced pressure. Precipitation from a THF–hexane (1:1) mixture afforded 0.11 g (18%) of the product as a very pale yellow solid, dec pt >150 °C. IR (CH_2Cl_2): ν(CO) 1960 (s), 1855 (vs); $\nu(\mathrm{C}\underset{\cdots}{-}\mathrm{O})$ 1540 (m) cm^{-1}. ^{1}H NMR (CD_2Cl_2): τ 8.20 (m, 3, CH_2), 7.72 (s, 9, CH_3), 6.31 (m, 3, OCH_2), 2.45 (m, 60, C_6H_5). Anal. Calcd for $C_{81}H_{69}O_6N_2P_4Re\cdot{}^3/_4\,C_4H_8O$: C, 65.92; H, 4.94; N, 1.83. Found: C, 65.71; H, 4.85; N, 1.57.

General Preparation of the Anionic Bis(triacylmetalate) Complexes. To a stirred solution or suspension of 0.15–0.26 g of the appropriate acylpentacarbonyl complex in 50 mL of tetrahydrofuran at 0 °C was added 2 molar equiv of methyllithium as an ether solution. The reaction solution changed gradually to deep orange, and any undissolved acyl complex dissolved. The reaction was stirred for an additional 60 min and then was treated dropwise with a tetrahydrofuran solution of either aluminum trichloride or gallium trichloride (0.5 molar equiv). The reaction was stirred for an additional 1 h at 0 °C and then for 2 h at 25 °C. During this period the reaction solution changed gradually to amber. The reaction was then treated with either a solution of (PPN)BF_4 (0.5 molar equiv) in methylene chloride or solid tetramethylammonium tetrafluoroborate (0.5 molar equiv). The reaction was stirred for an additional 15–30 min. The solvent was removed under reduced pressure, and the reaction residue was extracted with methylene chloride. Precipitation from a methylene chloride/diethyl ether/alkane mixture afforded the products as white or pale yellow solids. The specific data for each complex are provided below.

Preparation of (PPN)[*fac*-$(OC)_3Re(CH_3CO)_3$]$_2$Al, 9. To a solution of 0.15 g (0.41 mmol) of **3** in 50 mL of THF was added 0.55 mL (0.94 mmol) of methyllithium (1.7 M) followed by the addition of a THF solution of 0.03 g (0.22 mmol) of $AlCl_3$ and a CH_2Cl_2 solution of 0.13 g (0.21 mmol) of (PPN)BF_4 affording, after crystallization from a CH_2Cl_2–heptane (4:1) mixture at −20 °C, 0.06 g (21%) of the product as a pale yellow solid, dec pt 240–265 °C. IR (CH_2Cl_2): ν(CO) 1990 (s), 1900 (vs); $\nu(\mathrm{C}\underset{\cdots}{-}\mathrm{O})$ 1485 (m) cm^{-1}. ^{1}H NMR (CD_2Cl_2): τ 7.49 (s, 18, CH_3), 2.41 (m, 30, C_6H_5). Anal. Calcd for $C_{54}H_{48}O_{12}NP_2Re_2Al$: C, 47.54; H, 3.55; N, 1.03; Re, 27.29; Al, 1.98. Found: C, 46.47; H, 3.56; N, 0.80; Re, 27.03; Al, 2.06.

Preparation of $[(CH_3)_4N]$[*fac*-$(OC)_3Re(CH_3CO)_3$]$_2$Al, 10. To a solution of 0.21 g (0.56 mmol) of **3** in 40 mL of THF was added 0.66 mL (1.12 mmol) of methyllithium (1.7 M) followed by the addition of a THF solution of 0.04 g (0.03 mmol) of $AlCl_3$ and 0.04 g (0.25 mmol) of $[(CH_3)_4N]BF_4$ affording, after crystallization from a CH_2Cl_2–heptane (1:1) mixture at −20 °C, 0.05 g (20%) of the product as an off-white solid, dec pt >205 °C. IR (CH_2Cl_2): ν(CO) 1990 (s), 1900 (vs); $\nu(\mathrm{C}\underset{\cdots}{-}\mathrm{O})$ 1485 (m) cm^{-1}. ^{1}H NMR (acetone-d_6): τ 7.50 (s, 18, CCH_3), 6.82 (s, 12, NCH_3). Anal. Calcd for $C_{22}H_{30}O_{12}NRe_2Al$: C, 29.36; H, 3.36; N, 1.56. Found: C, 29.22; H, 3.45; N, 1.15.

Preparation of (PPN){*fac*-$(OC)_3Re(CH_3CO)_2[(CH_3)_2CHCO]$}$_2$Al, 11. To a solution of 0.23 g (0.58 mmol) of isobutyrylpentacarbonylrhenium, **4**, in 50 mL of THF was added 0.50 mL (1.20 mmol) of methyllithium (2.4 M) followed by the addition of a THF solution of 0.04 g (0.30 mmol) of $AlCl_3$ and a CH_2Cl_2 solution of 0.19 g (0.30 mmol) of (PPN)BF_4 affording 0.08 g (21%) of the product as a very pale yellow solid, dec pt 191–194 °C. IR (CH_2Cl_2): ν(CO) 1985 (s), 1895 (vs); $\nu(\mathrm{C}\underset{\cdots}{-}\mathrm{O})$ 1490 (m) cm^{-1}. ^{1}H NMR (CD_2Cl_2): τ 9.29, 9.23, 9.19, 9.16, 9.12 (5 s, 12, $CH(CH_3)_2$); 7.47, 7.50, (2 s, 12, CH_3); 6.91 (m, 2, CH); 2.44 (m, 30, C_6H_5). Anal. Calcd for $C_{58}H_{56}O_{12}NP_2Re_2Al$: C, 49.04; H, 3.97; N, 0.99; Al, 1.90. Found: C, 49.07; H, 4.04; N, 1.00; Al, 1.76.

Preparation of (PPN)[*fac*-$(OC)_3Re(CH_3CO)_2(C_6H_5CH_2CO)$]$_2$Al, 12. To a stirred suspension of 0.20 g (0.45 mmol) of (phenylacetyl)pentacarbonylrhenium, **5**, in 50 mL of THF was added 0.50 mL (0.95 mmol) of methyllithium (1.9 M) followed by the addition of a THF solution of 0.03 g (0.22 mmol) of $AlCl_3$ and a CH_3Cl_2 solution of 0.14 g (0.22 mmol) of (PPN)BF_4 affording 0.09 g (27%) of the product as a pale yellow solid, dec pt 66–75 °C. IR (CH_2Cl_2): ν(CO) 1985 (s), 1895 (vs); $\nu(\mathrm{C}\underset{\cdots}{-}\mathrm{O})$ 1485 (m) cm^{-1}. ^{1}H NMR (CD_2Cl_2): τ 7.57, 7.56, 7.52 (3 s, 12, CH_3); 6.01, 6.04 (2 s, 4, CH_2); 2.49 (m, 40, C_6H_5). Anal. Calcd for $C_{66}H_{56}O_{12}NP_2Re_2Al$: C, 52.27; H, 3.72; N, 0.92. Found: C, 52.49; H, 4.42; N, 0.81.

Preparation of (PPN)[*fac*-$(OC)_3Re(CH_3CO)_3$]$_2$Ga, 13. To a solution of 0.20 g (0.55 mmol) of **3** in 50 mL of THF was added 0.43 mL (1.10 mmol) of methyllithium (2.6 M) followed by the addition of a THF solution of 0.05 g (0.28 mmol) of $GaCl_3$ and a CH_2Cl_2 solution of 0.18 g (0.29 mmol) of (PPN)BF_4 affording 0.13 g (32%) of the product as a white solid, dec pt 230–237 °C. IR (CH_2Cl_2): ν(CO) 1980 (s), 1897 (vs); $\nu(\mathrm{C}\underset{\cdots}{-}\mathrm{O})$ 1472 (m) cm^{-1}. ^{1}H NMR (CD_2Cl_2): τ 7.47 (s, 18, CH_3), 2.45 (m, 30, C_6H_5). Anal. Calcd for $C_{54}H_{48}O_{12}NP_2Re_2Ga$: C, 46.10; H, 3.44; N, 1.00. Found: C, 46.21; H, 3.73; N, 1.07.[7]

Preparation of (PPN){*fac*-$(OC)_3Re(CH_3CO)_2[(CH_3)_2CHCO]$}$_2$Ga, 14. To a solution of 0.21 g (0.52 mmol) of **4** in 40 mL of THF was added 0.50 mL (1.30 mmol) of methyllithium (2.6 M) followed by the addition of a THF solution of 0.05 g (0.28 mmol) of $GaCl_3$ and a CH_2Cl_2 solution of 0.16 g (0.26 mmol) of (PPN)BF_4 affording 0.08 g (21%) of the product as a pale yellow solid, dec pt 175–192 °C. IR (CH_2Cl_2): ν(CO) 1990 (s), 1897 (vs); $\nu(\mathrm{C}\underset{\cdots}{-}\mathrm{O})$ 1482 (m). ^{1}H NMR (CD_2Cl_2): τ 9.29, 9.28. 9.22, 9.21, 9.16 (5 s, 12, $CH(CH_3)_2$, J_{H-H} = 6.9 Hz); 7.51, 7.48 (2 s, 12, CH_3); 6.83 (complex multiplet, 2, CH, J_{H-H} = 6.9 Hz); 2.51 (m, 30, C_6H_5). Anal. Calcd for $C_{58}H_{56}O_{12}NP_2Re_2Ga$: C, 47.61; H, 3.86; N, 0.96. Found: C, 47.75; H, 3.95; N, 1.09.[7]

Preparation of (PPN)[*fac*-$(OC)_3Re(CH_3CO)_2(C_6H_5CH_2CO)$]$_2$Ga, 15. To a stirred suspension of 0.26 g (0.58 mmol) of **5** in 50 mL of THF was added 0.73 mL (1.16 mmol) of methyllithium (1.6 M) followed by the addition of a THF solution of 0.05 g (0.28 mmol) of $GaCl_3$ and a CH_2Cl_2 solution of 0.18 g (0.29 mmol) of (PPN)BF_4 affording 0.11 g (24%) of the product as a pale yellow solid, dec pt 65–87 °C. IR (CH_2Cl_2): ν(CO) 1990 (s), 1900 (vs); $\nu(\mathrm{C}\underset{\cdots}{-}\mathrm{O})$ 1475 (m) cm^{-1}. ^{1}H NMR (CD_2Cl_2): τ 7.54, 7.51, 7.48 (3 s, 12, CH_3); 5.93 (br, s, 4, CH_2); 2.46 (m, 40, C_6H_5). Anal. Calcd for $C_{66}H_{56}O_{12}NP_2Re_2Ga$: C, 50.84; H, 3.62; N, 0.90. Found: C, 49.46; H, 3.56; N, 1.08.[7]

General Preparation of the Neutral Bis(triacylmetalate) Complexes. To a stirred solution or suspension of 0.21–0.51 g of the acylpentacarbonylrhenium complex in 50 mL of tetrahydrofuran at 0 °C was added 2 molar equiv of methyllithium as an ether solution. The reaction solution changed gradually to deep orange, and any undissolved acyl complex disappeared. The reaction was stirred for an additional 1 h, and then a solution of either hafnium tetrachloride or zirconium tetrachloride (0.5 molar equiv) in tetrahydrofuran was added dropwise. The reaction was stirred for an additional 1 h at 0 °C and then 2 h at 25 °C. During this time period the reaction solution changed gradually to amber. The solvent was removed under reduced pressure, and the residue was extracted with benzene. The mixture was filtered and the solvent was removed from the filtrate at reduced pressure. Repeating the extraction procedure with toluene, followed by washing of the filtrate residue with several portions of pentane or hexane, we obtained the products as pale yellow solids.

Table I

R	M	*x*	*n*	compd
CH_3	PPN	1	0	**8**
CH_3	Al	3	−1	**9** and **10**
$CH(CH_3)_2$	Al	3	−1	**11**
$C_6H_5CH_2$	Al	3	−1	**12**
CH_3	Ga	3	−1	**13**
$CH(CH_3)_2$	Ga	3	−1	**14**
$C_6H_5CH_2$	Ga	3	−1	**15**
CH_3	Hf	4	0	**16**
$CH(CH_3)_2$	Hf	4	0	**17**
$C_6H_5CH_2$	Hf	4	0	**18**
CH_3	Zr	4	0	**19**
$(CH_2)_6/2$	Al	3	−1	**20**
$(CH_2)_7/2$	Al	3	−1	**21**

The specific data for each complex are provided below.

Preparation of [*fac*-$(OC)_3Re(CH_3CO)_3]_2Hf$, 16. To a solution of 0.51 g (1.38 mmol) of **3** in 50 mL of THF was added 2.05 mL (3.49 mmol) of methyllithium (1.7 M) followed by the addition of a THF solution of 0.22 g (0.69 mmol) of $HfCl_4$ affording 0.29 g (43%) of the product as a pale yellow solid, dec pt 120–200 °C. IR (CH_2Cl_2): $\nu(CO)$ 2020 (s), 1925 (vs); $\nu(C\overset{\cdots}{-}O)$ 1465 (m) cm^{-1}. ^1H NMR (acetone-d_6): τ 7.54 (s, CH_3). Anal. Calcd for $C_{18}H_{12}O_{12}Re_2Hf$: C, 22.12; H, 1.86; Re, 38.11. Found: C, 22.02; H, 2.16; Re, 37.05.[7]

Preparation of {*fac*-$(OC)_3Re(CH_3CO)_2[(CH_3)_2CHCO)]\}_2Hf$, 17. To a solution of 0.28 g (0.70 mmol) of **4** in 50 mL of THF was added 0.88 mL (1.40 mmol) of methyllithium (1.6 M) followed by the addition of a THF solution of 0.11 g (0.35 mmol) of $HfCl_4$ affording 0.08 g (11%) of the product as a pale yellow solid, dec pt >160 °C. IR (CH_2Cl_2): $\nu(CO)$ 2010 (s), 1918 (vs); $\nu(C\overset{\cdots}{-}O)$ 1470 (m) cm^{-1}. ^1H NMR (acetone-d_6): τ 9.21 (m, 12, $CH(CH_3)_2$), 7.61 (br, s, 12, CH_3), 6.45 (m, 2, CH). Anal. Calcd for $C_{22}H_{26}O_{12}Re_2Hf$: C, 25.57; H, 2.54. Found: C, 21.69; H, 2.78.[7]

Preparation of [*fac*-$(OC)_3Re(CH_3CO)_2(C_6H_5CH_2CO)]_2Hf$, 18. To a solution of 0.25 g (0.56 mmol) of **5** in 50 mL of THF was added 0.42 mL (1.09 mmol) of methyllithium (2.6 M) followed by the addition of a THF solution of 0.09 g (0.28 mmol) of $HfCl_4$ affording 0.13 g (21%) of the product as a pale yellow solid, dec pt 123–130 °C. IR (CH_2Cl_2): $\nu(CO)$ 2010 (s), 1920 (vs); $\nu(C\overset{\cdots}{-}O)$ 1473 (m) cm^{-1}. ^1H NMR ($CDCl_3$): τ 7.49 (br, s, 12, CH_3), 5.91 (br, s, 4, CH_2), 2.63 (m, 10, C_6H_5). Anal. Calcd for $C_{30}H_{26}O_{12}Re_2Hf$: C, 31.90; H, 2.32. Found: C, 29.28; H, 2.75.[7]

Preparation of [*fac*-$(OC)_3Re(CH_3CO)_3]_2Zr$, 19. To a solution of 0.21 g (0.57 mmol) of **3** in 50 mL of THF was added 0.45 mL (1.17 mmol) of methyllithium (2.6 M) followed by the addition of a THF solution of 0.07 g (0.30 mmol) of $ZrCl_4$ affording 0.05 g (10%) of the product as a pale yellow solid, dec pt >230 °C. IR (CH_2Cl_2): $\nu(CO)$ 2010 (s), 1922 (vs); $\nu(C\overset{\cdots}{-}O)$ 1470 (m) cm^{-1}. ^1H NMR (acetone-d_6): τ 7.58 (s, CH_3). Anal. Calcd for $C_{18}H_{18}O_{12}Re_2Hf$: C, 24.29; H, 2.04. Found: C, 21.76; H, 2.40.[7]

Results and Discussion

The general preparative procedure for the formation of the complexes of the triacylmetalate dianions is shown in Scheme I (see also Table I). This procedure involves the addition of 2 molar equiv of methyllithium to the acylpentacarbonylrhenium complex affording the triacylmetalate dianion. Although the manganese dianion [*fac*-$(PhCH_2CO)_3Mn(CO)_3]^{2-}$ was prepared previously in the presence of a 20-fold excess of $PhCH_2MgCl$,[8] the synthesis of these rhenium dianions occurs stoichiometrically and can be followed easily by IR. The addition of (PPN)Cl or a coordinating metal ion affords the triacylmetalate complexes.

Scheme I

$$RC(O)Re(CO)_5 + 2CH_3Li \xrightarrow[0\ ^\circ C]{THF} [fac\text{-}(OC)_3Re(RCO)(CH_3CO)_2]^{2-} \xrightarrow{{}^1/_2MCl_x} [fac\text{-}(OC)_3Re(RCO)(CH_3CO)_2]_2M^n$$

During the addition of the methyllithium solution, the carbonyl and acyl C–O stretching vibrations of the neutral acyl complex disappear with the concomitant appearance of the two-band $\nu(CO)$ pattern expected for the *fac* isomer of the dianion and a single $\nu(C\overset{\cdots}{-}O)$ band at much lower frequencies.

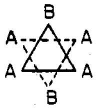
The dilithium salt of the triacetyl dianion, **1**, in THF solution has $\nu(CO)$ bands at 1957 and 1857 cm^{-1} with a relative intensity of ca. 1:2 and a $\nu(C\overset{\cdots}{-}O)$ band at 1532 cm^{-1}. These values represent an energy decrease of ca. 123 and 75 cm^{-1} from the respective oscillators of the acetylpentacarbonylrhenium complex upon the formation of the dianion. This trend is consistent with the increase of negative charge on the rhenium atom. A THF solution of the PPN salt of dianion **1** has $\nu(CO)$ bands at lower energy (1948 and 1844 cm^{-1}) and a $\nu(C\overset{\cdots}{-}O)$ band at higher energy (1552 cm^{-1}). These shifts reflect the coordination of the lithium ions to the dianion, **1**.[4] The PPN salt of **1** can be isolated as a solid as the THF solvate, **8**. This salt is stable in air for at least 24 h at 25 °C, and it decomposes upon heating above 150 °C. The proton NMR spectrum shows a sharp singlet at δ 2.28 for the three equivalent methyl groups.

The anionic bis-chelate complexes of aluminum and gallium, **9**–**15**, are white or pale yellow solids which can be isolated as the PPN or the tetramethylammonium (complex **10**) salts. These compounds are soluble in methylene chloride or THF but are insoluble in ether, alkanes, or aromatic solvents. These complexes are isolated in 20–32% yield, and they possess excellent thermal stability (dec pt 175–240 °C) except for the phenylacetyl complexes, **12** and **15**, which decompose thermally at 65–87 °C.

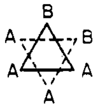
The infrared spectra in methylene chloride solution show two $\nu(CO)$ bands and one $\nu(C\overset{\cdots}{-}O)$ band at the average frequencies of 1987, 1898, and 1482 cm^{-1}, respectively. The shift of 38 cm^{-1} to higher energy for the weighted average of the $\nu(CO)$ bands of these complexes relative to that of the uncomplexed dianion **8** is consistent with a decrease in the electron density about the rhenium atom upon coordination of the dianion. The shift of 58 cm^{-1} to lower energy for the acyl $\nu(C\overset{\cdots}{-}O)$ band upon complexation is a diagnostic indication that the coordination complex has been formed.[4]

The proton NMR spectra also indicate that complexation has occurred. The average methyl resonance for the triacetylmetalate complexes, **9**, **10**, and **13**, in CD_2Cl_2 solution appears as a singlet at δ 2.52. A singlet resonance is consistent with the expected idealized D_{3d} symmetry of these complexes, and the downfield shift of 24 Hz from the methyl resonance frequency for the uncomplexed dianion, **8**, reflects the withdrawal of electron density from the rhenium moiety upon complexation. The proton NMR spectra of the unsymmetrically substituted ligands in the complexes, **11**, **12**, **14**, and **15**, should show the presence of any geometrical isomers. The observation of such isomerism is required for the confirmation of the solution-phase structure of these unique complexes.

For the unsymmetrical complexes having ligands possessing two identical and one different alkyl substituents, two geometrical isomers, **22** and **23**, are possible. The anti isomer has C_{2h} symmetry while the gauche isomer has only C_2 symmetry. For a given orientation of one complexed triacylmetalate ligand, the second ligand can coordinate to the metal ion forming the anti isomer or one of two statistically equivalent gauche isomers. The statistical equilibrium mixture would be $^1/_3$ anti and $^2/_3$ gauche.



22, anti



23, gauche

By use of the ligand substituents as probes for this isomerism, the proton NMR spectra should show the presence of

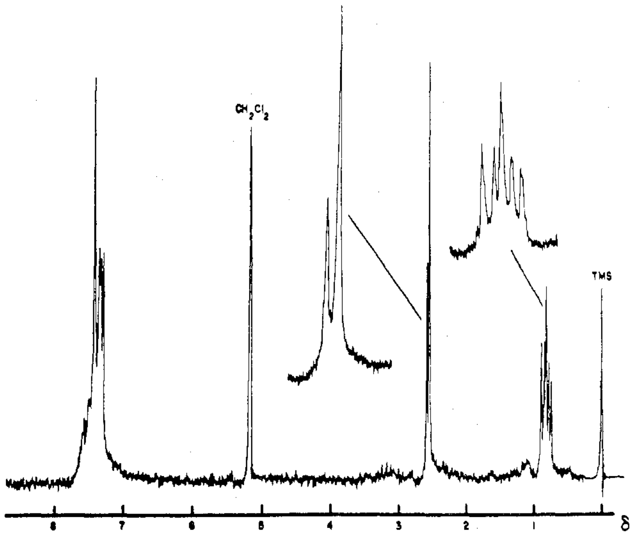


Figure 1. Complete proton NMR spectrum of (PPN){*fac*-$(OC)_3Re(CH_3CO)_2[(CH_3)_2CHCO]$}$_2$Al, **11**, in CD_2Cl_2 solution at 1080 Hz. The inserts are recorded at an expanded scale of 540 Hz.

isomers provided that the isomers are present in significant relative abundances, static on the NMR time scale, and exhibit sufficient anisochronism[9] to permit detection.

When A is methyl and B is isopropyl, the anti isomer would give a singlet for the four equivalent methyl substituents and a single doublet for the equivalent methyl groups of the isopropyl substituents. However, the gauche isomer would give two singlets of equal intensity for the methyl substituents and two doublets of equal intensity for the methyl groups of the isopropyl substituents since the methine carbon atom is now a prochiral center. If B is a phenylacetyl substituent, a similar analysis can be formulated. The best probes for this isomerism would be the methyl group resonances since these resonances are very sharp and intense.

Figure 1 shows the entire proton NMR spectrum of complex **11** in CD_2Cl_2 solution at 36 °C. The methyl resonances of the methyl and isopropyl substituents are shown in expanded scale as inserts. The methyl substituents appear as two singlets at δ 2.53 and 2.50 having a relative intensity of ca. 38:62, respectively. The larger peak, δ 2.50, splits into two singlets separated by 1 Hz upon further scale expansion. The methyl groups of the isopropyl substituents appear as five singlets centered at δ 0.81. The middle singlet appears to be approximately twice the intensity of any one of the other resonances.

This spectrum is consistent with the presence of anti and gauche isomers. The methyl substituents appear as three singlets with the weakest resonance, δ 2.53, being assigned to the anti isomer and the split resonance at δ 2.50 being assigned to the gauche isomer. The relative abundances may indicate a slight thermodynamic preference for the anti isomer although the error in integration may be considerable. The isopropyl resonances should show six resonances ideally. The observed five resonances are consistent with this expectation on the assumption of an accidental degeneracy of two of these resonances to form the peak of greatest intensity.

Figure 2 shows the methyl resonances of the methyl and isopropyl substituents of the complexes **12** (A), **14** (B), and **15** (C) in CD_2Cl_2 solution at various scale expansions. Spectrum A shows three singlets of unequal intensity for the methyl resonances. The assignment of the highest field resonance to the anti isomer and the other two more intense resonances to the gauche isomer is straightforward. Although peak overlap prevents accurate integration, the isomers appear to be present in nearly a statistical relative abundance. Apparently, the presence of the benzyl group induces a slightly larger anisochronism (4 Hz) between the methyl substituents of the gauche isomer than is observed in complex **11**.

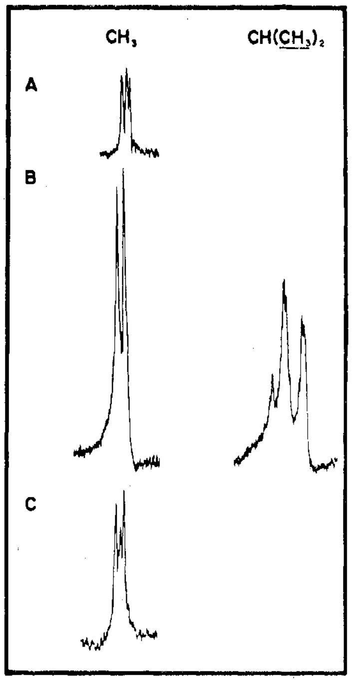


Figure 2. Expanded-scale methyl region of the proton NMR spectra of (PPN)[*fac*-$(OC)_3Re(CH_3CO)_2(C_6H_5CH_2CO)]_2$Al, **12** (A, 540 Hz), (PPN){*fac*-$(OC)_3Re(CH_3CO)_2[(CH_3)_2CHCO]$}$_2$Ga, **14** (B, 270 Hz), and (PPN)[*fac*-$(OC)_3Re(CH_3CO)_2(C_6H_5CH_2CO)]_2$Ga, **15** (C, 540 Hz), in CD_2Cl_2 solution.

Spectrum B shows only two singlets separated by 3 Hz for the methyl substituents indicating only a gauche isomer. The isopropyl methyl resonances give the expected doublet of doublets due to the prochirality at the methine carbon atoms of the gauche isomer. The anisochronism arising from this prochirality is 1 Hz. The peak at lowest field, δ 0.84, may be an impurity peak; however, if it represents half of the methyl doublet for the isopropyl group of the anti isomer, then an estimate of the relative anti isomer abundance is 32 ± 6%. The unobserved methyl substituent resonances of the anti isomer must then lie underneath the peak at δ 2.49. Although this assignment may be very speculative, there is no reason to assume that this gallium complex should exist as only the gauche isomer (see spectrum C).

Spectrum C shows three resonances for the methyl substituents centered at δ 2.49. The outer two resonances are of equal intensity, and they are assigned to the gauche isomer while the middle resonance is assigned to the anti isomer. Presumably, a nearly statistical relative isomer abundance is observed. Also, the rather large anisochronism (6 Hz) generated by the benzyl substituent is evident again.

The neutral bis-chelate complexes of hafnium and zirconium, **16**–**19**, are pale yellow air-sensitive solids which are insoluble in alkanes but are soluble in aromatic or polar organic solvents. These complexes are isolated in 10–43% yield, and they decompose thermally from 120 to 230 °C. Since these compounds would not crystallize from solution, it was very difficult to obtain a pure solid.[10] Some evidence of solution instability was also observed.

The infrared spectra in methylene chloride solution show the expected two-band ν(CO) pattern for a *fac*-$Re(CO)_3$ group. The average ν(CO) bands appear at 2013 and 1921 cm^{-1} which are ca. 24 cm^{-1} to higher energy than the corresponding bands of the anionic aluminum and gallium complexes. This shift is expected since these complexes bear an overall neutral charge. The average value of the $\nu(C\overset{-}{-}O)$ acyl bands is 1470 cm^{-1}. This band appears at lower energy than that of the uncomplexed dianion **8** or the anionic aluminum or gallium complexes by 82 and 12 cm^{-1}, respectively, which is consistent with the coordination of the triacylmetalate ligands to the group 4A metal ions.[4]

The proton NMR spectra are of poor quality owing to the solution instability and slight impurity of these compounds. The methyl substituent resonances of the triacetylhafnium and -zirconium complexes, **16** and **19**, appear at δ 2.46 and 2.42, respectively, in acetone-d_6 solution. These resonances appear ca. 16 Hz downfield from the methyl resonance of the uncomplexed dianion **8** which is consistent with complexation to the hafnium and zirconium ions.

Compounds **17** and **18** should exhibit geometrical isomerism; however, the poor quality of the spectra prevents this analysis. The peak width at half-height for the methyl substituent resonances of **17** and **18** are 16 and 12 Hz, respectively. Since the average separation of these resonances due to isomerization in the unsymmetrically substituted aluminum and gallium complexes, **11**, **12**, **14**, and **15**, is only 4 Hz, the observation of isomerism in **17** and **18** is not expected.

The aluminum compounds **20** and **21** are bis-chelate triacylmetalate complexes where the two metalla ligands are connected via a six- or seven-methylene bridge, respectively. These compounds are prepared with slightly more dilute solutions to favor the formation of a monomeric complex. Molecular models revealed that such complexes would exist only as the gauche isomer, and they would be, presumably, more stable in solution due to an imposed "chelate effect". Only the aluminum complexes were prepared, however, due to the inability to purify these compounds adequately. The complexes are very soluble in methylene chloride or THF, but they do not crystallize from solution.

The diacyl complexes **6** and **7** readily form the expected tetraacyl dianion (2067 (w), 1947 (br, vs), 1917 (sh, s), 1577 (m) cm^{-1}) and hexaacyl tetraanion (1952 (s), 1863 (vs), 1539 (m) cm^{-1}) when being treated with the stoichiometric amounts of methyllithium in THF solution. The aluminum complexes show the expected IR shifts (1989 (s), 1890 (vs), 1485 (m) cm^{-1}) due to complexation, and the proton NMR resonances of the methyl substituents appear as two singlets for the gauche isomer only at the expected frequencies (average values are δ 2.53 and 2.56). Because of the high solubility of these compounds and the observation of only the gauche isomer, these complexes are assumed to be either monomeric or dimeric in solution rather than a long-chain polymer. Further work with these bridged ligands is not planned.

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Registry No. **3**, 23319-44-0; **4**, 59831-00-4; **5**, 65312-81-4; **6**, 69439-94-7; **7**, 69439-95-8; **9**, 65337-55-5; **10**, 65274-13-7; **11**, gauche, 69493-70-5; **11**, anti, 69515-84-0; **12**, gauche, 69515-86-2; **12**, anti, 69493-81-8; **13**, 69493-72-7; **14**, gauche, 69515-60-2; **14**, anti, 69493-65-8; **15**, gauche, 69493-74-9; **15**, anti, 69576-01-8; **16**, 65319-76-8; **17**, 69454-62-2; **18**, 69439-98-1; **19**, 69439-99-2; **20**, gauche, 69508-46-9; **21**, gauche, 69493-67-0; $(PPN)_2[fac\text{-}(OC)_3Re(CH_3CO)_3]$, 69439-97-0; $NaRe(CO)_5$, 33634-75-2; suberyl dichloride, 10027-07-3; azelayl dichloride, 123-98-8; $AlCl_3$, 7446-70-0; $GaCl_3$, 13450-90-3.

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Phosphoranes. 9. Barrier to Exchange in $CF_3(CH_3)PF_3$. Comparison to Related Molecules Including $CF_3(CH_3)PCl_3$

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At reduced temperatures the directly bound F atoms in $CF_3(CH_3)PF_3$ are resolved into axial (two) and equatorial (one) environments. The barrier to fluorine permutation has been determined ($\Delta G^{\ddagger}_{298}$ = 8.8 kcal) from temperature-dependent ^{31}P (^1H-decoupled) and ^{19}F (CF_3 region) NMR spectroscopies. Comparing this barrier to those in similar trifluorophosphoranes with monodentate substituents suggests that the barrier to F permutation in $(CF_3)_2PF_3$ is very low (1–3 kcal), accounting the long-established inability to observe distinct F environments in this compound by NMR techniques. The behavior of $CF_3(CH_3)PCl_3$ which, in contrast to $CF_3(CH_3)PF_3$, exhibits pronounced temperature dependence of $^2J_{PF}$ and ϕ_{CF_3} suggests that the exchange process in the chloride is different from that of the fluoride. Spectroscopic characterization of $CF_3(CH_3)PF_3$, $CF_3(CH_3)PCl_3$, and the anion $CF_3(CH_3)PO_2^-$, formed by hydrolysis of both halides, is reported.

Introduction

Barriers to fluorine permutational exchange for a variety of trifluorophosphoranes with monodentate substituents[1-4] range from 6 to 20 kcal. The observed equivalence of F atoms in $(CF_3)_2PF_3$ even at very low temperatures has been interpreted in terms of D_{3h} molecular symmetry with two freely rotating axial CF_3 groups, a structure which violates the "electronegativity" rule.[5] NMR (^{19}F and ^{13}C)[6,7] data suggest that the appropriate ground-state structure of $(CF_3)_2PF_3$ has essentially C_{2v} symmetry with two CF_3 groups in the equatorial plane. We report herein the barrier for fluorine exchange in the related trifluorophosphorane $CF_3(CH_3)PF_3$ which, when compared to previously reported barriers for X_2PF_3 molecules, provides an insight to the behavior of $(CF_3)_2PF_3$.

Results and Discussion

^{19}F NMR spectra of the directly bound fluorine atoms of $CF_3(CH_3)PF_3$, illustrated in Figure 1, show typical fast-exchange behavior at ~300 K resolving to distinct fluorine environments (in a 2:1 intensity ratio) at 163 K. The pattern

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