Communications

Synthesis of the Trimetallic Manganese and Rhenium Complexes: $N[CH_2(\eta^5\text{-}C_5H_4)M(CO)_3]_3$. Derivatives of the Nonadentate "TCp" Ligand, Tris(cyclopentadienylmethyl)amine Trianion

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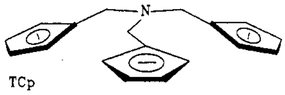
Summary: The title complexes are assembled by treating $N(CH_2Cl)_3$ with $(\eta^5\text{-}C_5H_4MgI)M(CO)_3$ to yield $TCp[M(CO)_3]_3$ ($TCp = N[CH_2(C_5H_4)]_3{}^{3-}$) (M = Mn (68%), Re (22%)). The TCp ligand is both thermally and photochemically robust such that the tetrahydrofuran- (THF-) substituted complex $TCp[Mn(CO)_2(THF)]_3$ can be cleanly prepared and further derivatized.

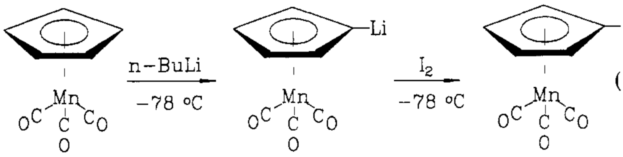
Polynuclear complexes whose metal centers are connected by bridging carbocyclic ligands are being actively sought to promote metal–metal interactions by holding the metals in close proximity.[1-6] Intramolecular metal cooperativity can lead to unique reactivities that deviate from mononuclear behavior.[2] Recent work has concentrated on fulvalene,[2,3] linked bis(cyclopentadienyl)[4] and tris(cyclopentadienyl)[5] ligands, and cyclopentadienyl (Cp) rings α-functionalized with donor ligands.[6] We wished to synthesize a bridging ligand that would hold *three* metals in close proximity and provide high stability as well as structural and synthetic flexibility. Such a ligand is tris(cyclopentadienylmethyl)amine trianion (TCp):



TCp

The Cp rings of TCp should provide strong anchoring of the metal centers to the bridging ligand and allow incorporation of a broad range of metal complexes. The nitrogen provides a fast inversion center with strong bonds to adjacent carbon. The methylene groups of this ligand are critical for allowing all three metals to interact. While two metals can interact if connected through bis(cyclopentadienyl) ligands linked by CH_2 or $Si(CH_3)_2$,[4] inducing three metals to interact requires longer "arms" from the central atom to avoid contact between the Cp α-hydrogens. Herein we report the synthesis of this ligand, tris(cyclopentadienylmethyl)amine (TCp), as its manganese and rhenium carbonyl trimetallic complexes. Preliminary results of their properties and reactivities are presented.

Cymantrene (20.3 mmol), dissolved in dry THF (100 mL) and under a N_2 atmosphere, is cooled to −78 °C in a dry ice–acetone bath and deprotonated by addition of 1.1 equiv of *n*-BuLi in hexanes.[6] After 25 min, a THF solution (60 mL) of iodine (20.3 mmol) that is precooled to −78 °C is added by cannula over 5 min. Warming to room temperature over 4 h is followed by rotary evaporation to a dark oil. Short path vacuum distillation (0.1 Torr) affords $ICpMn(CO)_3$ as a yellow oil which crystallizes on standing (66%) (eq 1).[7]



(1)

Cymantrenylmagnesium iodide is prepared from iodocymantrene following Rausch's procedure.[8] This Grignard solution is decanted from solid residues and cooled to 0 °C. A THF solution containing an equivalent of $N(CH_2Cl)_3$[10] is added dropwise to the Grignard. The solution is stirred for 12 h, followed by rotary evaporation of THF. The crude product is purified by preparative silica thin-layer chromatography (23 × 25 cm plate, 20 g of Fischer Scientific GF-TLC silica, eluant 10:10:1 benzene/hexane/ethyl acetate). The second yellow band gives a 68% yield of $TCp[Mn(CO)_3]_3$ (eq 2).[11]

The infrared spectrum of $TCp[Mn(CO)_3]_3$ in the carbonyl region closely matches that of the structurally similar monometallic complex $(\eta^5\text{-}C_5H_4Me)Mn(CO)_3$. The Cp ring protons give rise to a single resonance in the ^1H NMR which is again similar to that of methylcymantrene. At −85 °C, the methylene ^1H resonances (300 MHz) of $TCp[Mn(CO)_3]_3$ remain singlets, indicating that either the TCp ligand assumes a conformation where all methylenes are equivalent or interconversion of conformers with inequivalent methylenes is still fast on the NMR time scale at this temperature. The ^{13}C NMR spectrum of TCp-

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[7] This procedure is the preferred route to $(\eta^5\text{-}C_5H_4I)Mn(CO)_3$ in comparison with previous methods.[8,9]

[8] Kovar, R. F.; Rausch, M. D. *J. Org. Chem.* **1973**, *38*, 1918.

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[10] *Caution*: Protective clothing should be worn when handling $N(CH_2Cl)_3$ to avoid contact with skin. Fluck, E.; Meiser, P. *Angew. Chem., Int. Ed. Engl.* 1971, *10*, 653.

[11] $\mathbf{N[CH_2(C_5H_4)Mn(CO)_3]_3}$: IR ($cm^{-1}$, hexanes, $\nu(CO)$) 2026 (m), 1950 (s); ^1H NMR ($CDCl_3$) δ 4.71 (s, 12, C_5H_4), 3.30 (s, 6, CH_2); ^{13}C NMR ($CDCl_3$) δ 224.6 (s, CO) [100.9 (s), 83.9 (d, J_{CH} = 180 Hz), 82.3 (d, J_{CH} = 176 Hz), C_5H_4R], 50.9 (t, J_{CH} = 135 Hz, CH_2). Anal. Calcd for $C_{27}H_{18}Mn_3NO_9$: C, 48.75; H, 2.73; Mn, 24.77; N, 2.11. Found: C, 48.57; H, 2.78; Mn, 24.60; N, 2.19.

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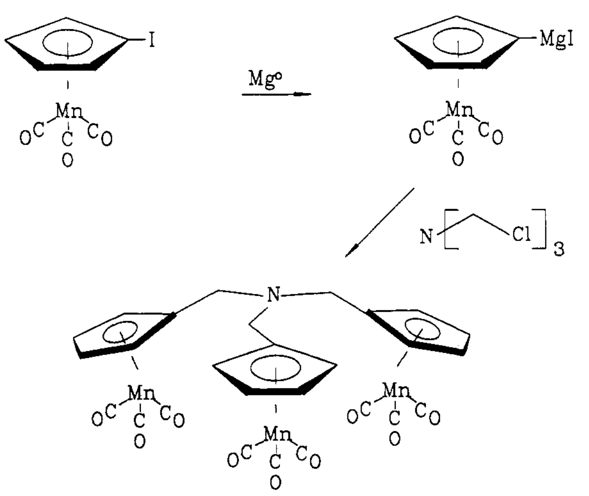
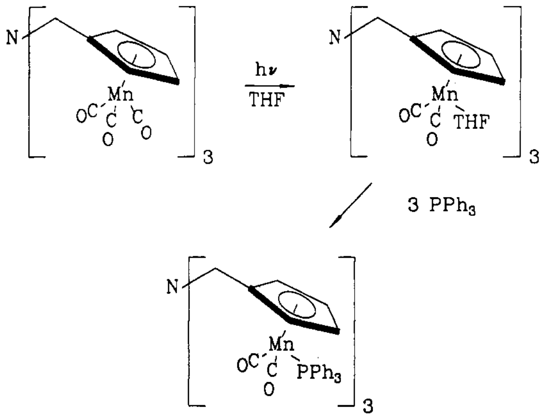


(2)

$[Mn(CO)_3]_3$ shows three chemically distinct carbons in the Cp ring resulting from ring substitution. The melting point for $TCp[Mn(CO)_3]_3$ in an evacuated capillary is 97–98 °C though no visible change in the yellow melt occurs until ca. 260 °C when it begins to darken.

Irradiation of $TCp[Mn(CO)_3]_3$ in THF at −90 °C with a 100-W mercury lamp generates $TCp[Mn(CO)_2(THF)]_3$[12] cleanly based on the IR spectrum. Obtaining the THF derivative subjects this TCp manganese trimer to the extraordinarily rich chemistry[12] of the $CpMn(CO)_2$ fragment. As a preliminary test, $TCp[Mn(CO)_2(THF)]_3$ was treated with a twofold excess of PPh_3 which gave $TCp[Mn(CO)_2(PPh_3)]_3$ in 35% unoptimized yield (eq 3).[13] Purification was performed by preparative TLC as described above for $TCp[Mn(CO)_3]_3$ but in the inert atmosphere of a glovebox eluting with 20% ethyl acetate in hexane.



(3)

In a manner analogous to that for $(\eta^5-C_5H_4I)Mn(CO)_3$, $(\eta^5-C_5H_4I)Re(CO)_3$ was prepared as a tan solid (89%) from $(\eta^5-C_5H_5)Re(CO)_3$ (0.63 mmol), n-BuLi in hexanes (0.65 mmol), and iodine (0.65 mmol).[14] The Grignard reagent $(C_5H_4MgI)Re(CO)_3$ is formed from $(C_5H_4I)Re(CO)_3$ (0.35 mmol) and excess magnesium dust as performed above for the manganese analogue. The Grignard is then combined with $N(CH_2Cl)_3$[10] (0.12 mmol) to obtain the trirhenium TCp complex $TCp[Re(CO)_3]_3$[15] in 22% yield also following the method used for $TCp[Mn(CO)_3]_3$.

Three or more Cp rings in a single molecule appear in an unusual collection of substances: metal sulfide cubanes,[16] f-element complexes,[17] and numerous metal clusters.[18] Our continuing studies are aimed at generalizing syntheses to TCp analogues of these compounds and exploring the effects of TCp on their reactivities.

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[12] Caulton, K. G. *Coord. Chem. Rev.* **1981**, *38*, 1. Fong, R. H.; Hersh, W. H. *Organometallics* **1985**, *4*, 1468.

[13] **$N[CH_2(C_5H_4)Mn(CO)_2PPh_3]_3$**: IR ($cm^{-1}$, THF, $\nu(CO)$) 1933 (s), 1870 (s); ^1H NMR ($CDCl_3$) δ 7.5–7.3 (m, 45, C_6H_5), 4.27 (br, 6, Cp), 4.07 (br, 6, Cp), 3.17 (br, 6, CH_2); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 232.5 (d, J_{CP} = 24 Hz, CO), 138.3 (d, J_{CP} = 40 Hz), 132.9 (d, J_{CP} = 10 Hz), 128.9 (d, J_{CP} = 82 Hz), 128.1 (d, J_{CP} = 9 Hz), 98.1 (s), 83.5 (s), 83.3 (s), 50.9 (s); $^{31}P\{^1H\}$ NMR (C_6D_6, relative to PPh_3 at δ −6.0) δ 92.3 (s). Anal. Calcd for $C_{78}H_{63}Mn_3NO_6P_3$: C, 68.48; H, 4.64. Found: C, 68.94; H, 5.22.

[14] This is the preferred route to $(\eta^5-C_5H_4I)Re(CO)_3$ when compared to other literature methods: Herrmann, W. A. *Chem. Ber.* **1978**, *111*, 2458.

[15] **$N[CH_2(C_5H_4)Re(CO)_3]_3$**: IR ($cm^{-1}$, hexanes, $\nu(CO)$) 2029 m, 1945 s; ^1H NMR ($CDCl_3$) δ 5.33 (s, 12, C_5H_4), 3.45 (s, 6, CH_2); ^{13}C NMR ($CDCl_3$) δ 193.6 (s, CO) [104.5 (s), 84.8 (d, J_{CH} = 179 Hz), 84.4 (d, J_{CH} = 184 Hz), C_5H_4R], 50.5 (t, J_{CH} = 137 Hz, CH_2). Anal. Calcd for $C_{27}H_{18}NO_9Re_3$: C, 30.62; H, 1.71. Found: C, 30.32; H, 1.74.

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Photodegradation of Poly(dialkylsilane)s in Solution: The Persistent Radicals Have an Unexpected Structure

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Summary: The structure of the initial persistent radicals observed upon UV irradiation of poly(dialkylsilane)s $(R_2Si)_n$ in solution, at any wavelength absorbed, is $-SiR_2-\dot{S}iR-SiR_2-$ as determined by EPR and ENDOR spectroscopy. A mechanism proposed for their formation consists of several steps, initiated by a new photochemical chain-breaking process, reductive elimination on a Si–Si–C unit, with the formation of trialkylsilyl terminal groups. The presence of such terminal groups in the irradiated product was established by GC–MS analysis after exhaustive irradiation at 254 nm.

Polysilanes[2] $(RR'Si)_n$ are of interest as photoresists.[3,4] They photodegrade both in the neat solid[4,5] and in solu-

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