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Metal Carbonyl Complexes of the Trindenyl Ligand: Crystal Structure of *trans*-$[Re(CO)_3]_3$(trindenyl)

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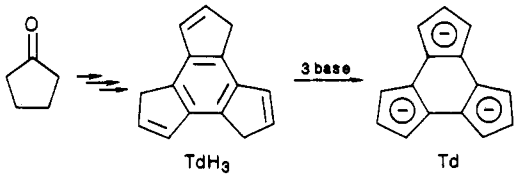
Dihydro-1*H*-trindene (TdH_3) was deprotonated with 3 mol equiv of KH and combined with 3 mol equiv of $Mn(CO)_3(NC_5H_5)_2Br$ yielding the trimetallic complex *trans*-$[Mn(CO)_3]_3$(Td) in 58% yield. The rhenium analogue *trans*-$[Re(CO)_3]_3$(Td) was prepared by a similar procedure in 74% yield utilizing $[Re(CO)_3(THF)Br]_2$ as the $Re(CO)_3^+$ source. The crystal structure of *trans*-$[Re(CO)_3]_3$(Td) has been determined: triclinic, $P\bar{1}$; $a = 6.990$ (3) Å, $b = 11.099$ (5) Å, $c = 15.264$ (8) Å; $\alpha = 82.52$ (4)°, $\beta = 79.13$ (4)°, $\gamma = 89.82$ (4)°; $V = 1152.8$ (9) Å^3; $Z = 2$; $R(F) = 4.29\%$. The two cyclopentadienyl rings to which the adjacent Re atoms are bonded are bent out of the trindenyl plane by 9.7 and 11.5°. The carbonyl ligands on these same rhenium atoms are maximally staggered. The bonds between the cyclopentadienyl rings have an average distance of 1.45 Å. The mono- and dirhenium trindenyl complexes $[Re(CO)_3]_n(Td)H_{3-n}$ ($n = 1$, 2) were also selectively synthesized. The diheterotrimetallic complex *trans*-$[Re(CO)_3]_2[Rh(CO)_2]$(Td) containing juxtaposed Re and Rh carbonyl groups was prepared in 71% yield by combining the thallium salt of the dirhenium complex *trans*-$[Re(CO)_3]_2Tl$(Td) with $[Rh(CO)_2Cl]_2$.

Introduction

Metal atoms that are held in close proximity exhibit unique properties such as reversible oxygen binding,[1] electron transport,[2] and carbon monoxide reduction.[3] Many ligand designs are being tested[4,5] for their propensity to hold two or more metal sites together in an effort to either mimic biologically active metal sites[6] or to search for new chemical[7] or physical[8] behavior. These systems differ from transition-metal clusters in that they do not require direct metal–metal bonds that often cleave and lead to cluster fragmentation.[9] The trindenyl trianion (Td) is a rigid polycyclic hydrocarbon consisting of three conjugated cyclopentadienyl (Cp) rings that may be useful as a di- and trinucleating ligand. Katz and Slusarek[10] first synthesized the trindenyl trianion in four steps from cyclopentanone (eq 1) and prepared the sandwich complex bis(trindene)diiron from the trindene dianion and ferrous chloride.



(1)

We wished to explore the propensity of the trindenyl trianion to act as a nonadentate ligand that would force at least two metal sites to be juxtaposed. We report here that both manganese and rhenium form trimetallic trindenyl complexes. Several products containing one or two rhenium tricarbonyl units per Td ligand have also been prepared selectively. Further, two *different* metals (Re, Rh) were bonded to the same trindenyl ligand by a rational synthetic route such that they are rigidly held in close proximity. Below we describe the synthesis and characterization of these trindenyl complexes and the molecular structure of the trirhenium trindenyl complex. A preliminary account of this work has been reported.[11]

Results and Discussion

The trindenylmanganese trimer *trans*-$[Mn(CO)_3]_3$Td was readily prepared in 58% yield by combining dihydro-1*H*-trindene (TdH_3, two isomers), KH, and $Mn(CO)_3(py)_2Br$ (py = pyridine) under mild conditions (eq 2). The rhenium analogue *trans*-$[Re(CO)_3]_3$Td was synthesized in a similar manner from $[Re(CO)_3(THF)Br]_2$ in 74% yield. Treating dihydro-1*H*-trindene with KH and then $Mn(CO)_5Br$ as the $Mn(CO)_3^+$ source gave only $Mn_2(CO)_{10}$ under the reducing conditions of the reaction. Both *trans*-$[Mn(CO)_3]_3$Td and *trans*-$[Re(CO)_3]_3$Td have

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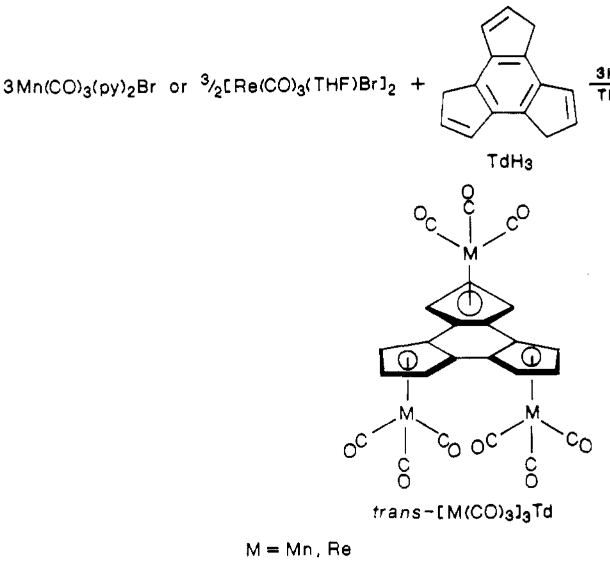

(2)

low solubility in benzene, acetone, methylene chloride, and chloroform (e.g. <3 mg/mL) but dissolve well in THF (ca. 20 mg/mL). They are both air stable as solids, and only *trans*-$[Mn(CO)_3]_3Td$ is slightly air sensitive in solution.

Spectroscopic data for these and the other trindenylmetal complexes described below are listed in Tables I and II. In particular, the ^{13}C NMR spectrum of *trans*-$[Re(CO)_3]_3Td$ contained the eight unique carbon atoms of the trindenyl ligand but only one carbonyl resonance where two were expected. To clarify this point, a low-temperature ^{13}C NMR spectrum was obtained. The CO resonance grew a shoulder at low temperature, and by −80 °C two distinct resonances were observed that integrated in a ratio of 1:2 (195.2, 195.3 ppm). Since no broadening of the signals was observed, this divergence of resonances is attributed to temperature dependence of the chemical shifts for the two kinds of CO on the two cis rhenium sites versus the trans rhenium atom. The IR spectra of both *trans*-$[Mn(CO)_3]_3Td$ and *trans*-$[Re(CO)_3]_3Td$ showed vibrational coupling[5] of the carbonyls on the two metal atoms that are rigidly held on the same side of the trindenyl plane.

The trindenyl ligand is unique in its ability to bind three metals through Cp rings and to force at least two of these in close proximity. The molecular structure of *trans*-$[Re(CO)_3]_3Td$ was undertaken to better understand the bonding and the metal group interactions in a representative trindenylmetal trimer (Figure 1). The Cp rings bound to the cis rhenium atoms are bent out of the plane of the central ring by 9.7 and 11.5°. This bending appears to result from steric repulsion between the cis rhenium carbonyl moieties. All intramolecular nonbonded distances are longer by 0.2 Å than the shortest intermolecular contacts. This suggests that crowding is not important with the Cp rings bent out of the central ring plane to this extent. The magnitude of this bending is in the same range as the bending between Cp rings of the fulvalene ligand in several complexes that contain metal–metal bonds (e.g. $(Fv)(Cp)_2Mo_2H_3^+$,[12] $(Fv)W_2(CO)_6$;[13] Fv = fulvalene).[14] The cis $Re(CO)_3$ groups show maximal staggering of their carbonyl ligands (Figure 2). The C–C bond lengths *between* the Cp rings have an average distance of 1.45 Å, perhaps indicating slight conjugation throughout the trindenyl ligand. Both the structural and ^{13}C NMR data[15] indicate essentially planar η^5 coordination of all three metals to the trindenyl ligand.

Table I. ^1H NMR Spectral Data for Trindenylmetal Carbonyls[a]

compd	cyclopentadienyl protons
trans-$[Mn(CO)_3]_3Td$	5.75 (d, 2 H, J = 4.7), 5.50 (d, 2 H, J = 3.2), 5.32 (d, 2 H, J = 4.9), 5.22 (t, 1 H, J = 3.0), 4.90 (t, 2 H, J = 3.0)
trans-$[Re(CO)_3]_3Td$	6.47 (dd, 2 H, J = 1.4, 2.9), 6.13 (d, 2 H, J = 2.9), 5.99 (dd, 2 H, J = 1.4, 2.9), 5.90 (t, 1 H, J = 2.8), 5.55 (t, 2 H, J = 2.9)
trans-$[Re(CO)_3]_2[Rh(CO)_2]Td$	6.52 (dd, 1 H, J = 1.5, 2.9), 6.32 (t, 1 H, J = 2.5), 6.16 (d, 2 H, J = 2.9), 6.06 (dd, 1 H, J = 1.5, 2.3), 6.00 (t, 1 H, J = 2.3), 5.96 (m, 1 H), 5.87 (t, 1 H, J = 2.9), 5.56 (t, 1 H, J = 2.9)
trans-$[Re(CO)_3]_2TdH$[b]	5.85 (dd, 1 H, J = 1.5, 2.9), 5.83 (dd, 1 H, J = 1.4, 2.8), 5.82 (dd, 1 H, J = 1.4, 2.8), 5.72 (dd, 1 H, J = 1.5, 2.7), 5.63 (t, 1 H, J = 3.1), 5.62 (t, 1 H, J = 3.0)
$[Re(CO)_3]TdH_2$[c]	5.88–5.85 (m, 1 H), 5.78–5.75 (m, 1 H), 5.71–5.67 (m, 1 H)

[a] Chemical shifts are reported in ppm downfield of TMS in THF-d_8 (J values in Hz) except where noted. [b] Chloroform-d solvent. Vinyl, 6.90 (td, 1 H, J = 1.6, 5.5), 6.71 (td, 1 H, J = 1.5, 5.5); methylene, 3.53 (td, 1 H, J = 1.5, 24.0), 3.46 (td, 1 H, J = 1.5, 24.0). [c] Chloroform-d solvent. Vinyl, 7.21–6.93 (m, 2 H), 6.73–6.61 (m, 2 H); methylene, 3.49–3.38 (m, 4 H).

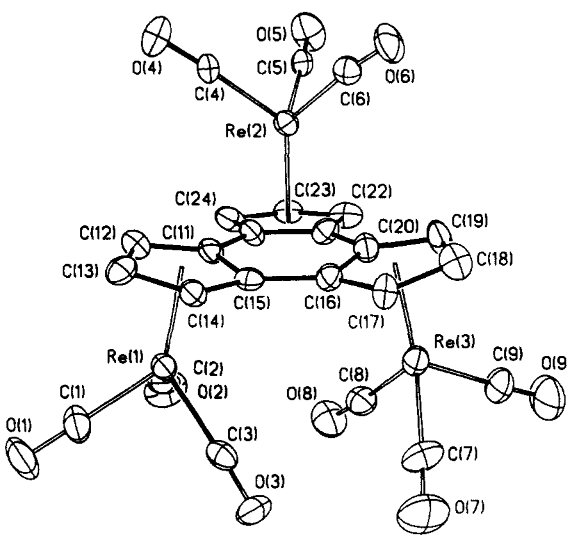

Figure 1. Structure of *trans*-$[Re(CO)_3]_3Td$ showing the atom-labeling scheme. Hydrogen atoms have been deleted here and in Figure 2.

The facile trindenylrhenium synthesis is well-suited to searching for other reaction products and isomers. It was important to establish whether mono- and dimetallotrindenes could be each selectively synthesized. To this end, dihydro-1*H*-trindene was treated with a deficiency of base and rhenium reagent. The monorhenium trindenyl complex $[Re(CO)_3]TdH_2$ was prepared in a fair yield by way of the tin derivative $(Me_3Sn)TdH_2$. Dihydro-1*H*-trindene was sequentially treated with 1 equiv of *n*-BuLi, 1 equiv

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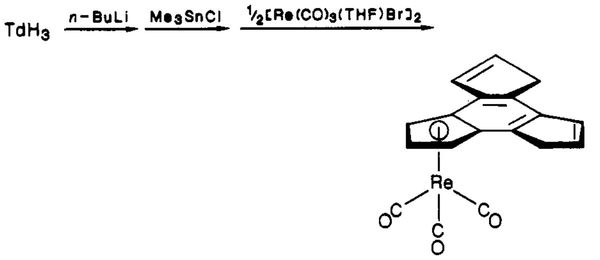
Table II. Infrared[a] and ^{13}C NMR[b] Spectral Data for Trindenylmetal Carbonyls

compd	IR (rel abs)	^{13}CO	cyclopentadienyl carbons
trans-$[Mn(CO)_3]_3Td$	2032 (0.4), 2020 (1.0), 1955 (0.7), 1938 (1.0)	225.2, 225.1 (sh)	97.5, 96.7, 95.0, 86.0, 82.1, 81.8, 77.2, 74.9
trans-$[Re(CO)_3]_3Td$	2034 (0.3), 2022 (0.9), 1949 (0.6), 1931 (1.0)	194.4 (s)	99.3 (s), 98.9 (s), 97.3 (s), 89.0 (d), 84.6 (d), 83.2 (d), 77.8 (d), 77.0 (d)
trans-$[Re(CO)_3]_2[Rh(CO)_2]Td$	2049 (0.3), 2019 (0.6), 1989 (0.3), 1931 (1.0)	195.2, 194.5, 190.1 (d)[c]	108.6, 101.5, 99.9, 98.8, 98.4, 97.1, 93.4, 88.9, 85.0, 80.8 (2 C), 80.0, 76.4, 76.3, 76.1
trans-$[Re(CO)_3]_2TdH$[d]	2017 (0.7), 1927 (1.0)	193.3, 193.1	102.6, 99.5, 97.8, 95.9, 88.0, 87.9, 74.4, 73.1, 72.7, 72.5
$[Re(CO)_3TdH_2$[e]	2018 (0.8), 1920 (1.0)	194.0, 193.8, 193.6	106.2, 104.5, 102.9, 101.3, 90.3, 90.2, 90.1, 69.0, 68.7, 68.2, 67.91

[a] cm^{-1}, ν(CO), THF. [b] Chemical shifts are reported in ppm downfield of TMS in THF-d_8 (J values in Hz) except where noted. [c] J_{C-Rh} = 85 Hz. [d] Chloroform-*d* solvent. Vinyl, 136.5, 135.6, 133.4, 128.8 ppm; methylene, 39.6 ppm. [e] Chloroform-*d* solvent. Vinyl, 139.8, 138.3, 138.2, 137.2, 136.2, 135.2, 135.0, 134.5, 134.2, 133.9, 131.8, 130.1, 130.0, 129.4, 129.3 ppm; methylene, 39.1, 39.0, 38.9 ppm.

of Me_3SnCl, and 1/2 equiv of $[Re(CO)_3(THF)Br]_2$ affording $[Re(CO)_3]TdH_2$ in 45% yield (eq 3).

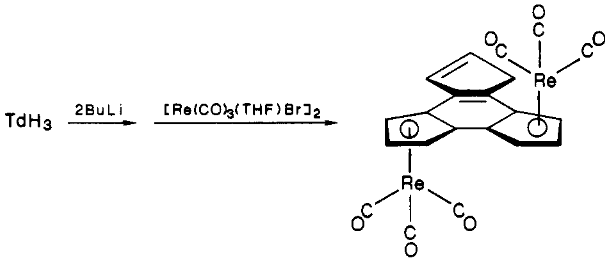


(3)

$[Re(CO)_3]TdH_2$

The monorhenium trindenyl complex exists as four isomers that differ only by the position of the two double bonds in the neutral five-membered rings. Two of these isomers are enantiomeric. Thirty-two of the thirty-four resonances predicted in the ^{13}C NMR spectrum are resolved and have the relative intensities expected for the statistical 1:2:1 distribution of distinguishable isomers. Proton resonances were not fully resolved, though integrations of the vinyl/Cp/methylene regions are 4:3:4, respectively, as predicted.

Combining a 1:2:1 mol ratio of dihydro-1*H*-trindene/*n*-BuLi/$[Re(CO)_3(THF)Br]_2$ yielded *trans*-$[Re(CO)_3]_2TdH$ in 22% yield and less than 5% each of other rhenium–trindene derivatives (eq 4). The trans isomer of the dirhenium trindene product was earlier[11] distinguished from the minor cis isomer by absence of vibrational coupling of carbonyls in the FTIR spectrum. Using an excess of rhenium reagent gave a similar yield. The predominance of *trans*-$[Re(CO)_3]_2TdH$ over *cis*-$[Re(CO)_3]_2TdH$ and the fact that *cis*-$[Re(CO)_3]_3Td$ has not been observed can be understood by steric repulsion between metal groups on the same side of the ligand as interpreted from the molecular structure. All isomers of $[Re(CO)_3]_nTdH_{3-n}$ (n = 1–3) have now been observed with the exception of *cis*-$[Re(CO)_3]_3Td$.



(4)

trans-$[Re(CO)_3]_2TdH$

The availability of *trans*-$[Re(CO)_3]_2TdH$ provides a useful structure to which a third *different* metal can be added, forcing a cis disposition of the heterometals. We have now prepared such a complex: The diheterotrimetallic compound *trans*-$[Re(CO)_3]_2[Rh(CO)_2]Td$ was prepared in 71% yield by treating *trans*-$[Re(CO)_3]_2TdH$ with TlOEt to form the thallium salt *trans*-$[Re(CO)_3]_2Tl(Td)$, followed by addition of $[Rh(CO)_2Cl]_2$ (eq 5).

In conclusion, we have explored the syntheses of manganese-, rhenium-, and rhodium-containing trindenyl

Table III. Crystal Data for $[Re(CO)_3]_3(Td)$

(a) Crystal Parameters

formula	$C_{24}H_9O_9Re_3$	γ, deg	89.82 (4)
fw	999.93	V, Å^3	1152.8 (9)
cryst system	triclinic	Z	2
space group	$P\bar{1}$	D(calc), g cm^{-1}	2.881
a, Å	6.990 (3)	μ(Mo Kα), cm^{-1}	166.7
b, Å	11.099 (5)	T, K	300
c, Å	15.264 (8)	size, mm	0.12 × 0.15 × 0.40
α, deg	82.52 (4)	T_{max}/T_{min}	2.54
β, deg	79.13 (4)		

(b) Data Collection

hkl collected	±8, ±12, ±17	indpdnt reflns (R_{int}, %)	5276 (7.07)
2θ scan limits, deg	4–55	obsd reflns ($F_o \geq 5\sigma$)	4043
scan type	Wyckoff	std reflns	3 std/197 reflns, <1% decay
reflns collected	5498		

(c) Structure Refinement

data/parameter	12.4	GOF	1.061
$R(F)$, %	4.29	Δ/σ(max)	0.025
$R(wF)$, %	4.86	$\Delta\rho$(max), e Å^{-3}	2.71, Re(1) noise

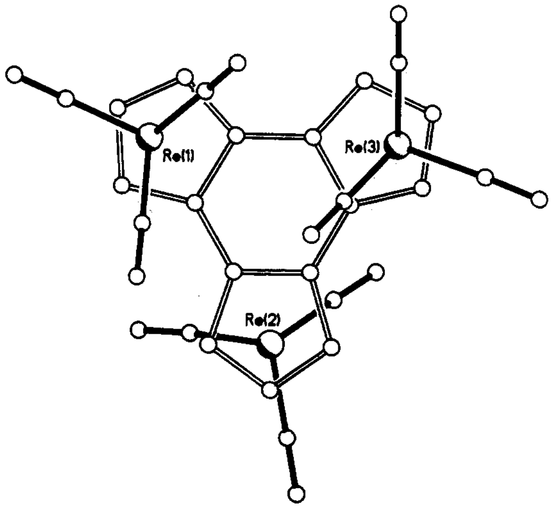
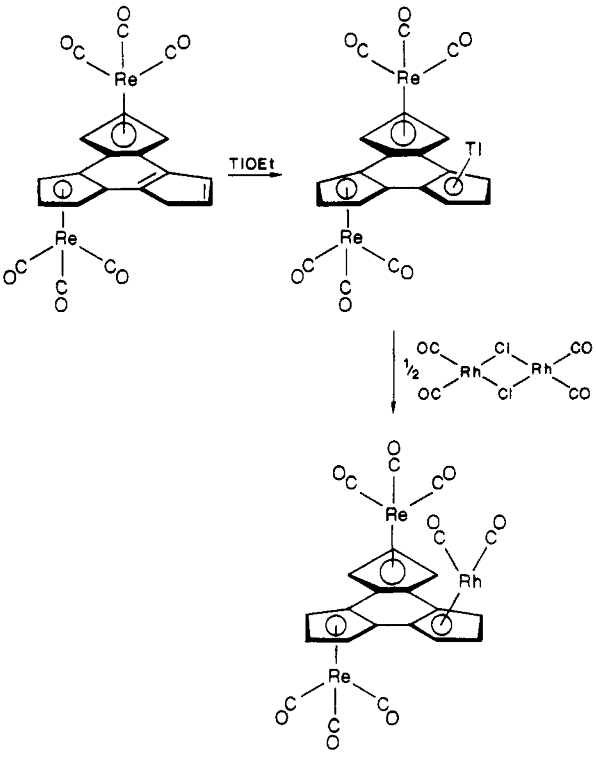


Figure 2. A planar projection of *trans*-$[Re(CO)_3]_3Td$ showing the relative arrangement of $Re(CO)_3$ groups.



(5)

trans-$[Re(CO)_3]_2[Rh(CO)_2]Td$

complexes through a variety of routes involving K^+, Li^+, Me_3Sn^+, and Tl^+ derivatives of trindenyl anions and find these to approximate the syntheses of Cp analogues. Collectivley, these provide convenient routes to compounds containing closely spaced metal atoms. These results suggest that a considerable range of other metallotrindenyl complexes should also be accessible. The preparation of these and exploration of their properties is the focus of our continuing research.

Experimental Section

General Methods. Benzene, tetrahydrofuran, and hexane were distilled from benzophenone ketyl. Methylene chloride was distilled from P_2O_5 and ethyl acetate was distilled before use. Dihydro-1*H*-trindene,[10] $Mn(CO)_3(NC_5H_5)_2Br$,[16]and $[Re(CO)_3(THF)Br]_2$[17] were prepared by literature methods. All reactions were performed under nitrogen by using Schlenk techniques or in a glovebox. Infrared spectra were recorded on a Perkin-Elmer 1800 FTIR. NMR and low-temperature NMR spectra were collected on General Electric QE-300 and GN-300 spectrometers. Mass spectral determinations were performed by the Midwest Center for Mass Spectrometry, a National Science Foundation Regional Instrumentation Facility (Grant No. CHE 8620177). Elemental analysis was performed by Schwarzkopf Microanalytical Laboratory and Dornis and Kolbe Microanalytical Laboratory, Mulheim, West Germany.

Preparation of *trans*-$[Mn(CO)_3]_3Td$. A 25-mL Schlenk flask was charged with 60 mg of dihydro-1*H*-trindene (0.31 mmol), 40 mg of KH (1.0 mmol), 4 mL of THF, and 379 mg of $Mn(CO)_3(py)_2Br$ (py = pyridine, 1.00 mmol) and the mixture stirred for 16 h. Approximately 100 mg of NH_4Cl was added, and the mixture was stirred for $^1/_2$ h and then centrifuged. The supernatant was decanted and the residue extracted with 2 mL of THF. The volume of the combined THF solutions was reduced until the solution became slightly cloudy (ca. 3 mL) and was allowed to stand 20 min under nitrogen. Solid $Mn(CO)_3(py)_2Br$ was removed by decanting the supernatant. Methylene chloride (2 mL) was added to the supernatant, and the volume was reduced to ca. 2 mL. After 20 min the precipitated *trans*-$[Mn(CO)_3]_3Td$ was collected, and the supernatant was saved. The *trans*-[Mn-

Table IV. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^3) for $[Re(CO)_3]_3(Td)$

	x	*y*	*z*	U^a
Re(1)	−684.1 (7)	7770.1 (4)	5468.0 (3)	37.4 (1)*
Re(2)	1397.1 (7)	3975.8 (4)	7942.6 (3)	35.4 (1)*
Re(3)	−2530.6 (7)	8305.3 (4)	8476.0 (3)	40.5 (2)*
Re(3′)	2607 (22)	8121 (13)	8572 (10)	36 (4)
O(1)	−817 (21)	8704 (10)	3519 (7)	86 (5)*
O(2)	−3954 (16)	5903 (10)	5576 (8)	78 (5)*
O(3)	−3628 (14)	9718 (8)	6048 (6)	60 (3)*
O(4)	4914 (16)	3418 (11)	6516 (7)	75 (4)*
O(5)	1524 (18)	1369 (8)	8856 (7)	76 (5)*
O(6)	3778 (14)	4963 (10)	9188 (7)	64 (4)*
O(7)	−3832 (20)	10846 (10)	7873 (10)	98 (6)*
O(8)	−5276 (14)	7109 (10)	7505 (7)	68 (4)*
O(9)	−5708 (21)	8112 (16)	10193 (8)	117 (7)*
C(1)	−808 (22)	8348 (13)	4245 (8)	56 (5)*
C(2)	−2753 (17)	6632 (11)	5538 (9)	48 (4)*
C(3)	−2530 (17)	8982 (10)	5846 (8)	42 (4)*
C(4)	3639 (18)	3663 (11)	7077 (7)	46 (4)*
C(5)	1520 (17)	2339 (11)	8522 (7)	43 (4)*
C(6)	2979 (19)	4560 (11)	8701 (8)	45 (4)*
C(7)	−3439 (21)	9913 (13)	8099 (11)	61 (5)*
C(8)	−4332 (17)	7577 (13)	7867 (9)	52 (4)*
C(9)	−4483 (24)	8207 (18)	9534 (10)	76 (7)*
C(11)	868 (16)	6429 (9)	6419 (7)	35 (3)*
C(12)	1882 (19)	6453 (11)	5501 (8)	47 (4)*
C(13)	2618 (17)	7662 (13)	5211 (9)	50 (4)*
C(14)	2094 (16)	8387 (10)	5909 (7)	37 (3)*
C(15)	1018 (15)	7629 (9)	6681 (7)	35 (3)*
C(16)	443 (15)	7814 (11)	7610 (7)	39 (4)*
C(17)	748 (18)	8813 (11)	8068 (7)	43 (4)*
C(18)	363 (19)	8398 (12)	9028 (8)	51 (4)*
C(19)	−278 (21)	7200 (12)	9133 (8)	53 (5)*
C(20)	−271 (16)	6809 (11)	8287 (7)	40 (4)*
C(21)	−673 (16)	5643 (9)	8005 (7)	38 (3)*
C(22)	−1690 (16)	4544 (10)	8478 (9)	44 (4)*
C(23)	−1822 (18)	3738 (11)	7856 (9)	48 (4)*
C(24)	−802 (20)	4265 (12)	6992 (9)	52 (5)*
C(25)	−96 (18)	5454 (10)	7082 (7)	41 (4)*

[a] Parameters with an asterisk are equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table V. Selected Bond Distances and Angles for $[Re(CO)_3]_3Td$

(a) Bond Distances (Å)			
Re(1)–CNT(1)[a]	1.978 (11)	Re(3)–CNT(3)	1.977 (13)
Re(1)–C(1)	1.911 (13)	Re(3)–C(7)	1.945 (14)
Re(1)–C(2)	1.902 (12)	Re(3)–C(8)	1.936 (14)
Re(1)–C(3)	1.928 (11)	Re(3)–C(9)	1.899 (15)
Re(1)–C(11)	2.350 (11)	Re(3)–C(16)	2.347 (10)
Re(1)–C(12)	2.314 (13)	Re(3)–C(17)	2.310 (12)
Re(1)–C(13)	2.273 (12)	Re(3)–C(18)	2.341 (14)
Re(1)–C(14)	2.305 (12)	Re(3)–C(19)	2.292 (14)
Re(1)–C(15)	2.372 (12)	Re(3)–C(20)	2.296 (12)
Re(2)–CNT(2)	1.965 (12)	C(1)–O(1)	1.128 (16)
Re(2)–C(4)	1.912 (11)	C(2)–O(2)	1.156 (17)
Re(2)–C(5)	1.923 (12)	C(3)–O(3)	1.151 (15)
Re(2)–C(6)	1.915 (14)	C(4)–O(4)	1.172 (15)
Re(2)–C(21)	2.346 (11)	C(5)–O(5)	1.129 (15)
Re(2)–C(22)	2.276 (11)	C(6)–O(6)	1.144 (18)
Re(2)–C(23)	2.297 (13)	C(7)–O(7)	1.099 (18)
Re(2)–C(24)	2.300 (15)	C(8)–O(8)	1.107 (18)
Re(2)–C(25)	2.335 (12)	C(9)–O(9)	1.185 (19)
(b) Bond Angle Ranges (deg)			
Re–C–O- (range)	174 (1)–178 (1)	pentagonal C–C–C- (range)	107 (1)–110 (1)
hexagonal C–C–C- (range)	119 (1)–120 (1)	CNT–Re–C- (range)	121.8 (5)–127.3 (6)
C–Re–C- (range)	88.4 (6)–91.8 (7)		

[a] CNT = centroid of five-membered ring.

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Table VI. Least-Squares Planes for $[Re(CO)_3]_3Td$

	atom	dev, Å	atom	dev, Å
plane 1	C(11)	0.059	C(20)	0.064
	C(15)	−0.030	C(21)	−0.034
	C(16)	−0.032	C(25)	−0.027
plane 2	C(11)	−0.005	C(14)	−0.007
	C(12)	0.001	C(15)	0.008
	C(13)	0.004		
plane 3	C(16)	0.022	C(19)	−0.003
	C(17)	−0.024	C(20)	−0.012
	C(18)	0.016		
plane 4	C(21)	−0.013	C(24)	0.009
	C(22)	0.019	C(25)	0.003
	C(23)	−0.018		

Interplanar Angles (deg)

1–2	9.7	1–4	−8.8
1–3	11.5		

$(CO)_3]_3Td$ was redissolved in 2 mL of THF followed by 2 mL of CH_2Cl_2. The volume was again reduced to ca. 2 mL and allowed to stand 20 min. The solid *trans*-$[Mn(CO)_3]_3Td$ was again collected, and solvents were removed from the combined THF/CH_2Cl_2 supernatants. The residue was dissolved in a minimum of THF, and crystallization was induced by addition of an equal volume of CH_2Cl_2 as before. Several crops of crystals were collected and recrystallized in this manner. The solid was vacuum dried affording 110 mg of *trans*-$[Mn(CO)_3]_3Td$ (58%). HRMS (FAB): calcd for M^+ $C_{24}H_9Mn_3O_9$ *m/e* 605.8388, found 605.8394. Anal. Calcd for *trans*-$[Mn(CO)_3]_3Td$ ($C_{24}H_9Mn_3O_9$): C, 47.56; H, 1.50. Found: C, 47.41; H, 1.62.

Preparation of *trans*-$[Re(CO)_3]_3Td$. Dihydro-1*H*-trindene (50 mg, 0.26 mmol), $[Re(CO)_3(THF)Br]_2$ (330 mg, 0.391 mmol), and KH (36 mg, 0.90 mmol) were combined and stirred in 6 mL of THF for 12 h. The reaction mixture was stirred with excess NH_4Cl for 10 min and then centrifuged. The solvent was removed from the supernatant, and the white residue was washed with CH_2Cl_2. The crude product was recrystallized from THF by evaporation and then washed with CH_2Cl_2. This gave 188 mg (72%, 0.188 mmol) of *trans*-$[Re(CO)_3]_3Td$. Preparative TLC of the combined CH_2Cl_2 washes, eluted with 1:3 ethyl acetate/hexane, yielded three fractions. These were recovered in the following order of decreasing mobility: *trans*-$[Re(CO)_3]_2TdH$ (10 mg, 0.013 mmol, 5%), *trans*-$[Re(CO)_3]_3Td$ (6 mg, 0.006 mmol, 2%), and *cis*-$[Re(CO)_3]_2TdH$[11] (3 mg, 0.004 mmol, 2%). Anal. Calcd for *trans*-$[Re(CO)_3]_3Td$ ($C_{24}H_9O_9Re_3$): C, 28.83; H, 0.91. Found: C, 29.21; H, 1.01.

Preparation of $[Re(CO)_3]TdH_2$. A 10-mL Schlenk flask, charged with dihydro-1*H*-trindene (70 mg, 0.36 mmol) and THF (3 mL), was cooled to −78 °C, and *n*-BuLi in hexanes (0.14 mL, 0.36 mmol) was added dropwise with stirring. The solution immediately turned yellow and then orange. After 10 min Me_3SnCl (ca. 100 mg, 0.50 mmol) was added. The cold bath was removed until the color became a pale yellow. The reaction mixture was recooled to −78 °C, and $[Re(CO)_3(THF)Br]_2$ (200 mg, 0.237 mmol) was added. The cold bath was removed, and the mixture was stirred for 4 h. The supernatant was reduced to 1 mL by vacuum, applied to a preparative TLC plate, and eluted with 1:2 hexane/benzene. The major fraction was $[Re(CO)_3]TdH_2$ ($R_f = 0.7$, 75 mg, 45%). HRMS (FAB): calcd for M^+ $C_{18}H_{11}O_3Re_1$ *m/e* 460.0239, found 460.0226. Anal. Cald for $[Re(CO)_3]TdH_2$ ($C_{18}H_{11}O_3Re_1$): C, 46.85; H, 2.40. Found: C, 46.76; H, 2.46.

Preparation of *trans*-$[Re(CO)_3]_2TdH$. A 10-mL Schlenk flask containing a stirbar was charged with 50 mg of dihydro-1*H*-trindene (0.26 mmol) and 2 mL of THF and then cooled to −78 °C. *n*-Butyllithium in hexanes (0.20 mL, 0.52 mmol) was added to the solution and stirred 2 min before the cold bath was removed for 15 min. The solution became cloudy orange. Then $[Re(CO)_3(THF)Br]_2$ (242 mg, 0.28 mmol) was delivered. The reaction mixture was allowed to warm to room temperature. Stirring was continued for 3 h. The sample was handled in air from this point. After centrifugation, the supernatant was evaporated to dryness and the residue was redissolved in ca. $^3/_4$ mL of CH_2Cl_2 and applied to a silica preparative TLC plate which was eluted with 1:2 benzene/hexane. The major fraction (R_f = 0.3) was *trans*-$[Re(CO)_3]_2TdH$ (42 mg, 22%). HRMS (FAB): calcd for M^+ $C_{21}H_{10}O_6Re_2$ *m/e* 729.9566, found 729.9539. Anal. Calcd for $[Re(CO)_3]_2TdH$ ($C_{21}H_{10}O_6Re_2$): C, 34.52; H, 1.38. Found: C, 34.65; H, 1.26.

Preparation of *trans*-$[Re(CO)_3]_2[Rh(CO)_2]Td$. A solution of *trans*-$[Re(CO)_3]_2TdH$ (18 mg, 0.025 mmol) in 1.5 mL of THF was added to an 8-mL flask under nitrogen containing an excess of TlOEt (29 mg, 0.12 mmol) and shaken for 2 min. Then $[Rh(CO)_2Cl]_2$ (Strem Chemical Co., 20 mg, 0.05 mmol) was added slowly over 5 min. After 30 min the solution was passed through a short silica gel column and eluted with THF. The crude product was applied to a silica preparative TLC plate with THF and eluted with 4:1:1 hexane/ethyl acetate/benzene. The most mobile fraction was yellow-orange, affording 16 mg of *trans*-$[Re(CO)_3]_2[Rh(CO)_2]Td$ (71%). HRMS (FAB): calcd for ($M^+ - CO$) $C_{22}H_9O_7Re_2Rh_1$ *m/e* 859.8492, found 859.8473. Anal. Calcd for *trans*-$[Re(CO)_3]_2[Rh(CO)_2]Td$ ($C_{23}H_9O_8Re_2Rh_1$): C, 31.09; H, 1.02. Found: C, 30.83; H, 0.88.

Crystal Structure Determination. Collection of Diffraction Data. A colorless crystal of *trans*-$[Re(CO)_3]_3(Td)$ was mounted on a glass fiber with epoxy cement. Unit-cell parameters were determined through least-squares refinement of the angular settings for 25 reflections ($20 \leq 2\theta \leq 25°$). Data were collected on a Nicolet R3m/μ diffractometer with graphite monochromator (λ(Mo Kα) = 0.71073 Å). An empirical absorption correction (six reflections, ψ scan, 216 data) was applied to the data collected. Crystal data are listed in Table III.

Structure Solution and Refinement. The structure was solved by direct methods (SOLV) which located the Re atoms. The remaining non-hydrogen atoms were located through subsequent Fourier syntheses and least-squares refinement. An alternate position for Re(3), Re(3′), trans to Re(3), was located and refined isotropically to a final occupancy factor of 0.030 (1). The occupancies of Re(3) and Re(3′) were constrained to a combined occupancy of one. None of the lighter atoms associated with Re(3′) were discernible in difference maps. All non-hydrogen atoms except Re(3′) were anisotropically refined. Carbon(5), which become "non-positive definite" on final refinement, had its off-diagonal thermal parameters automatically set to zero by the refinement program. All hydrogen atoms were calculated and fixed to ideal isotropic positions.

All programs used are from the P3 (Nicolet XRD, Madison, WI) and SHELXTL (Sheldrick, 1984, V.5.1) program libraries. Table IV contains atomic coordinates; Table V lists selected bond lengths and angles.

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Supplementary Material Available: Tables of bond lengths and angles, anisotropic thermal parameters, and hydrogen atom coordinates (4 pages); a listing of structure factors (24 pages). Ordering information is given on any current masthead page.