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Polymetallic compounds of extended polyaromatic ligands. Rhenium and manganese carbonyl derivatives of truxene

Theodore L. Tisch, Thomas J. Lynch * and Raul Dominguez
Department of Chemistry, University of Nevada, Reno, NV 89557 (U.S.A.)

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Abstract

Truxene was deprotonated with KH in the presence of $Mn(CO)_3(pyridine)_2Br$ to yield truxenyl-manganese adducts with one, two or three $Mn(CO)_3{}^+$ units bound to the five-membered rings of the truxenyl ligand. These could also be prepared through haptotropic rearrangements of arene-coordinated $Mn(CO)_3{}^+$ (i.e. $[Mn(CO)_3]_n(\eta^6\text{-truxene})^{n+}$, $n = 1, 2, 3$). The *cis* isomer of the dimanganese carbonyl truxene complex, $[Mn(CO)_3]_2(\eta^5\text{-truxenyl})$ was synthesized only through this latter route. Mono-, di- and tri-rhenium carbonyl derivatives were prepared by treating truxene with KH then $[Re(CO)_3(THF)Br]_2$. All metallotruxenes were air sensitive, thermally stable and were characterized by FT-IR, ^1H and ^{13}C NMR and field desorption mass spectrometry. These results are presented in terms of providing guidelines for the design of polymetallic macromolecules.

Introduction

The chemistry of metals bound to aromatic compounds is among the most extensively studied areas of organometallic chemistry. Benzene and the cyclopentadienyl (Cp) anion, along with their derivatives, are the most thoroughly examined [1]. In contrast, relatively little extension has been made from these simple compounds to the coordinating ability of extended polycyclic aromatics [2]. Understanding of such systems would relate to known and anticipated bulk properties of polymeric conductors [3], molecular electronics [4], electrode films [5], multi-metal catalysts [6], organometallic polymers [7] and metal-polymer interfaces. In light of this, we decided to explore techniques for introducing several metal sites onto large polycyclic aromatics and to determine the stability and reactivity properties of such materials.

Truxene (10,15-dihydro-5H-tribenzo[a,f,k]trindene, TxH_3) [8] was an attractive polycyclic aromatic on which to focus our initial studies for several reasons: it is easily synthesized (i.e. one step from the commercially available indanone in 81%

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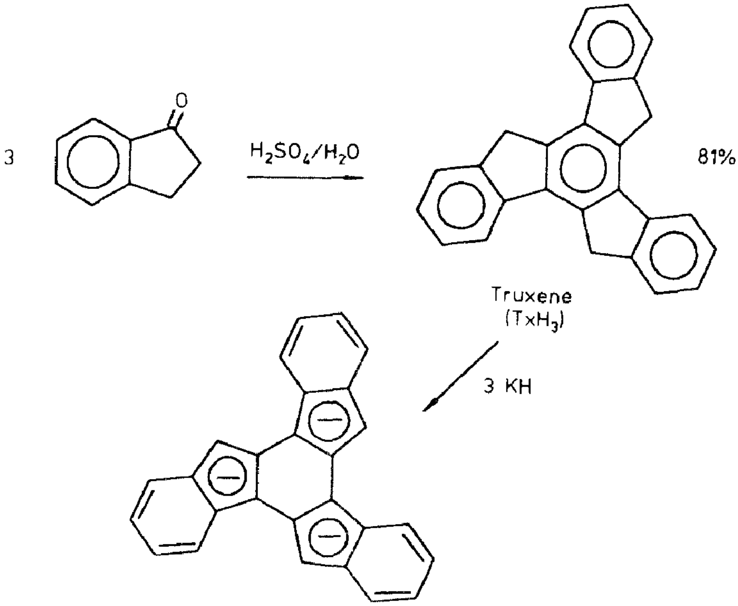


(1)

yield) and is stable in air to high temperature (> 325 °C) (eq. 1). The truxene trianion is formed by treating TxH_3 with three equivalents of base [8]. Truxene has four benzene rings and three Cp rings in its trianion form that are all potential sites for metal and multi-metal binding. Because of its size, metal complexes of the truxenyl ligand may be considered a bridge between mononuclear and polymeric organometallic compounds.

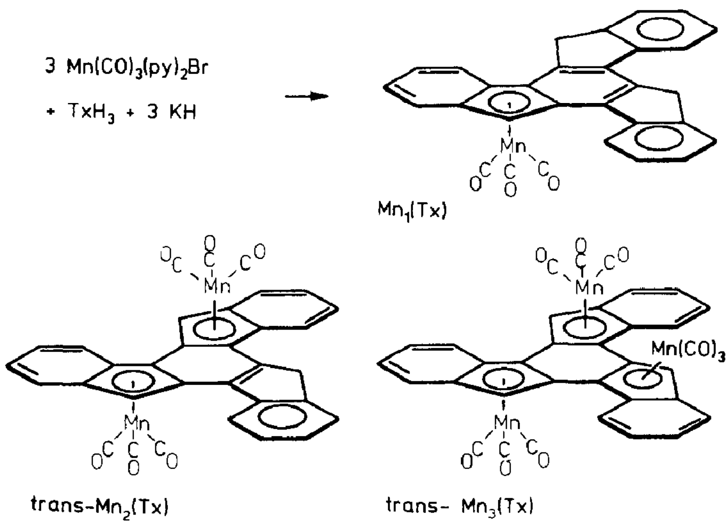
Herein we report the synthesis and characterization of seven metallotruxenes through two different synthetic routes utilizing both Cp and arene rings and a preliminary evaluation of their physical properties.

Results and discussion

Manganese carbonyl complexes of truxene

Deprotonation of truxene occurred upon reaction with potassium hydride and a catalytic amount of potassium t-butoxide in THF to form the stable truxene trianion. The truxene methylene ^1H NMR singlet at 4.27 ppm (6H) diminished as a new singlet due to the trianion methine appeared at 6.64 ppm. The structure and stability of the truxenyl anions suggested that polymetallic complexes of truxene could be prepared directly.

Two routes have been explored for synthesizing manganese truxene derivatives. The first (Method A) involved the reaction of truxene with 3 equiv. of KH and 3 equiv. of $Mn(CO)_3(py)_2Br$ (py = pyridine) in THF (eq. 2). Since all three reagents were combined, the manganese reagent presumably reacted with the truxene mono- and di-anions as they formed such that the trianion was never present in appreciable concentration. Ammonium chloride was added to the reaction mixture after no further change was observed in the carbonyl region of the FT-IR spectrum to protonate residual truxenyl anions.



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Extensive trials on purification of product mixtures were performed. Preparative thin layer chromatography [10] (TLC) was found to be the best method for separation of these macromolecules. Chromatographic fractions highly enriched in each product were collected though analytically pure samples could not be obtained. Column chromatography, fractional crystallization and high pressure liquid chromatography were attempted but gave inferior results. This is, most likely, a consequence of both the structural similarity and low solubility of the manganese carbonyl truxenes. Arnold et al. found similar purification obstacles of oligomeric metallocenes in a recent report [11]. The resulting metallotruxenes were characterized by FT-IR, ^{1}H and ^{13}C NMR and field desorption mass spectrometry (FD-MS) and identified as $Mn_1(Tx)$, *trans*-$Mn_2(Tx)$, and *trans*-$Mn_3(Tx)$ (eq. 2). The spectroscopic data for all new compounds are collected in Tables 1, 2 and 3.

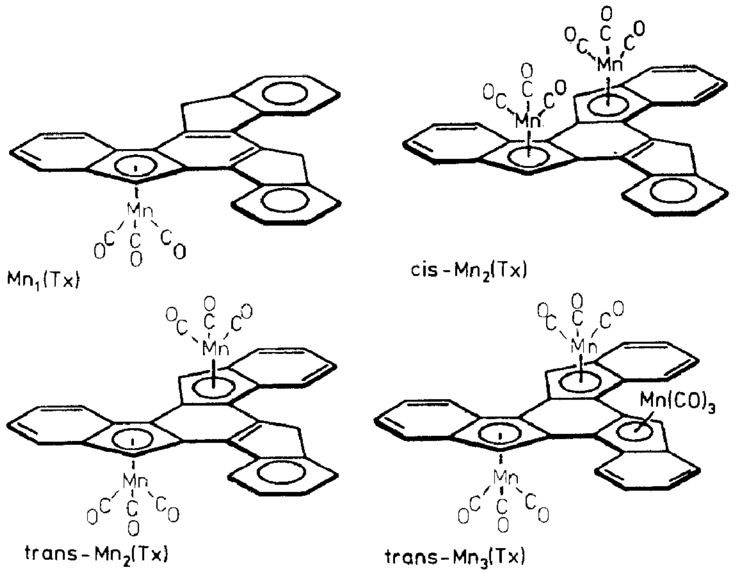
Methine protons of the manganese truxenes resonate in the distinct region of 5.9–6.3 ppm. The chemical shifts of the methylene protons of the mono- and di-manganese truxenyl complexes are also distinct for each derivative, appearing as AB quartets with ^{1}H–^{1}H couplings of ca. 22 Hz. The methine carbons of the three metallotruxenes resonate between 59.2 and 66.5 ppm in the ^{13}C NMR spectra. The methylene carbons of the mono- and di-substituted metallotruxenes resonate at ca. 37 ppm; close to the value found for truxene itself (36.6 ppm). Earlier characterization of $Mn(CO)_3(\eta^5$-fluorenyl) was useful in these assignments [12,13].

Both $Mn_1(Tx)$ and *trans*-$Mn_2(Tx)$ have two carbonyl IR absorbances at ca. 2015 and 1935 cm^{-1}. The FT-IR spectrum of *trans*-$Mn_3(Tx)$ is more complicated (see below). The parent ions for $Mn_1(Tx)$, *trans*-$Mn_2(Tx)$ and *trans*-$Mn_3(Tx)$ were observed by FD-MS. The close match between the calculated and observed parent ion isotropic abundances confirm their stoichiometries (Table 3).

The second route to manganese truxenes (Method B) proceeded through arene-bonded $[Mn(CO)_3]_n(\eta^6\text{-truxene})^{n+}$ ($n = 1, 2, 3$) cations formed by combining truxene, a Lewis acid ($AlCl_3$) and $Mn(CO)_5Br$ in refluxing 1,2-dichloroethane (eq. 3). These synthetic intermediates were not isolated but observed by FT-IR [14*].

Deprotonation of $[Mn(CO)_3]_n(\eta^6\text{-truxene})^{n+}$ methylenes with 1,8-bis(dimethylamino)naphthalene created cyclohexadienylmanganese units on the truxenyl ligand.

$$TxH_3 + AlCl_3 + Mn(CO)_5Br \xrightarrow[\text{(ii) proton sponge}]{\text{(i) reflux 15 h}}$$



$Mn_1(Tx)$ cis-$Mn_2(Tx)$ trans-$Mn_2(Tx)$ trans-$Mn_3(Tx)$ (3)

The manganese tricarbonyl groups were then induced to migrate to the five-membered rings by heating, referred to as haptotropic rearrangements [15]. This synthesis follows the route described by Treichel to form fluorenylmanganese complexes [13]. After preparative TLC, four products were characterized as $Mn_1(Tx)$, *trans*-$Mn_2(Tx)$, *cis*-$Mn_2(Tx)$, and *trans*-$Mn_3(Tx)$. The distinction between *cis* and *trans* isomers of the dimanganese truxene complexes was made by their CO stretching frequencies in the FT-IR spectra. The *cis*-$Mn_2(Tx)$ isomer has vibrationally coupled carbonyls giving rise to four carbonyl absorptions (Table 3) [16]. This is in contrast to the two absorptions observed for isolated $Mn(CO)_3{}^+$ groups found in both $Mn_1(Tx)$ and *trans*-$Mn_2(Tx)$. This vibrational coupling was also seen for *trans*-Mn_3Tx as would be expected for two $Mn(CO)_3{}^+$ moieties in cisoid positions.

The product distributions from the two synthetic routes, A and B, differ most in the yield of *cis*-$Mn_2(Tx)$. Method B gave significant quantities of the *cis* dimanganese isomer, while none was isolated from Method A. This can be understood by considering that in Method B the manganese tricarbonyl units were first bonded to the arene rings. Two such manganese groups could bond to terminal arenes on the same side of truxene with no steric interference. The migration of both to inner five-membered rings would then provide a route to the sterically crowded *cis*-$Mn_2(Tx)$. This change in product distribution suggests that there is an energetically unfavorable barrier to *cis*-$Mn_2(Tx)$ by the route that attempted to bind two $Mn(CO)_3{}^+$ directly to the five-membered rings (Method A).

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* Reference number with asterisk indicates a note in the list of references.

Table 1

^{1}H NMR data for manganese and rhenium truxene complexes [a]

Compound	Aromatic	Methine	Methylene
Tx [b]	8.00 (s, br, 3H) 7.44 (s, br, 3H) 6.64 (s, br, 6H)	6.64 (s, 3H)	
Mn_1(Tx)	8.19–7.13 (m, 12H)	5.91 (s, 1H)	4.22 (AB, *J* 22.5 Hz $\Delta\nu$ 110.3 Hz) 3.99 (AB, *J* 22.2 Hz $\Delta\nu$ 41.9 Hz)
trans-Mn_2(Tx)	8.17–7.14 (m, 12H)	6.24 (s, 1H) 6.15 (s, 1H)	4.42 (AB, *J* 22.6 Hz $\Delta\nu$ 45.8 Hz)
cis-Mn_2(Tx)	8.17–7.13 (m, 12H)	6.22 (s, 1H) 5.77 (s, 1H)	4.13 (AB, *J* 22.4 Hz $\Delta\nu$ 98.3 Hz)
trans-Mn_3(Tx)	7.98–7.16 (m, 12H)	6.32 (s, 1H) 6.09 (s, 1H) 6.05 (s, 1H)	
Re_1(Tx)	8.23–7.21 (m, 12H)	6.26 (s, 1H)	4.06 (AB, *J* 22.5 Hz $\Delta\nu$ 84.6 Hz) 3.90 (AB, *J* 22.1 Hz $\Delta\nu$ 53.4 Hz)
trans-Re_2(Tx)	8.20–7.16 (m, 12H)	6.71 (s, 1H) 6.65 (s, 1H)	4.45 (AB, *J* 22.3 Hz $\Delta\nu$ 13.4 Hz)
trans-Re_3(Tx) [c]		6.86 (s, 1H) 6.55 (s, 1H) 6.53 (s, 1H)	

[a] 300 MHz, $CDCl_3$, ppm, chemical shifts measured downfield from TMS. [b] THF-d_8. [c] Aromatic resonances masked by those of Re_1(Tx) and *trans*-Re_2(Tx).

Table 2

$^{13}C\{^1H\}$ NMR data for manganese and rhenium complexes [a]

Compound	CO	Methine	Methylene
Tx [b]		84.0	
Mn_1(Tx) [c]	224.9	59.2	37.5, 36.3
trans-Mn_2(Tx) [c]	224.2	63.9 62.4	38.0
cis-Mn_2(Tx) [c]	225.0 224.3	66.5 64.0	38.1
Re_1(Tx)	192.6	57.3	37.1, 36.1
trans-Re_2(Tx)	192.3 192.2	62.7 61.3	37.6

[a] 75 MHz, THF-d_8, ppm. Arene carbon resonances of metallotruxenes are between 100 and 145 ppm. [b] Arene resonances: 102.7, 110.9, 114.0, 115.9, 117.6, 125.3, 132.3, 134.5 ppm. [c] $CDCl_3$.

Rhenium carbonyl complexes of truxenes

The truxenyl-rhenium carbonyl derivatives were prepared by combining truxene, KH and $[Re(CO)_3(THF)Br]_2$ in THF and stirring for 24 h (eq. 4). Addition of ammonium chloride protonated residual methine carbons. After removal of solvent and preparative TLC, the recovered yellow metallotruxenes were identified as Re_1(Tx), *trans*-Re_2(Tx) and *trans*-Re_3(Tx). The *cis*-dirhenium truxenyl complex was

Table 3

FT-IR and mass spectral data for manganese and rhenium truxene complexes

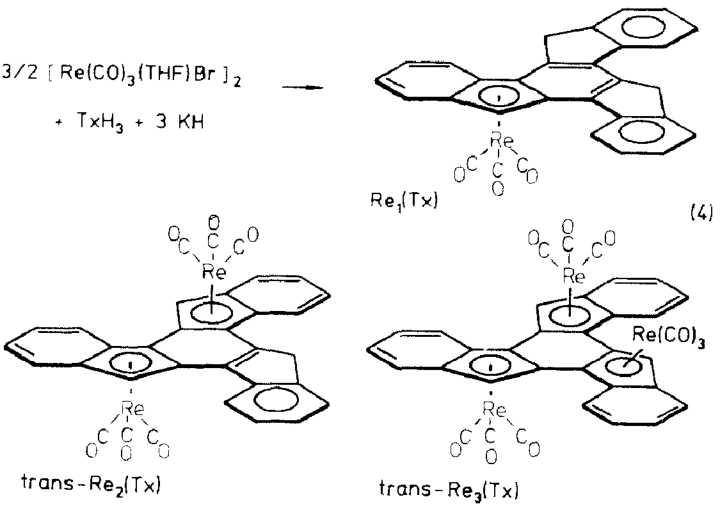
Compound	FT-IR ν(CO) [a]	MS, *m/e* (Found, (calcd. (%))
Mn_1(Tx)	2015 s, 1932 s, br	480(100, 100), 481(33, 34), 482(10, 6)
trans-Mn_2(Tx)	2015 s, 1939 s, br	618(100, 100), 619(39, 38), 620(7, 8)
cis-Mn_2(Tx)	2026 s, 2015 s, 1955 sh, 1931 s, br	618(100, 100), 619(39, 38), 620(7, 8)
trans-Mn_3(Tx)	2029 s, 2019 s, 1954 sh, 1938 s, br	756(100, 100), 757(47, 41), 758(16, 10)
Re_1(Tx)	2028 s, 1921 s, br	610(52, 58), 611(26, 20), 612(100, 100), 613(25, 33), 614(6, 5)
trans-Re_2(Tx)	2019 s, 1931 s, br	878(31, 29), 879(8, 11), 880(100, 100), 881 (38, 36), 882(88, 87), 883(31, 31), 884(5, 6)
trans-Re_3(Tx) [b]		1146(11, 11), 1147(8, 5), 1148(75, 58), 1149(24, 23), 1150(100, 100), 1151(33, 39), 1152(56, 61), 1153(21, 22), 1154(9, 4)

[a] THF, cm^{-1}. [b] FT-IR carbonyl absorbances were masked by those of Re_1(Tx) and *trans*-Re_2(Tx).

not observed which corroborates the results of the manganese truxenyl synthesis by Method A.

The ^1H and ^{13}C NMR and FT-IR data for the three rhenium truxenes compare well to those of the manganese truxenes with deviations expected for the change of metal centers. Field desorption mass spectra of the rhenium truxenes benefited from the two naturally occurring isotopes: ^{185}Re (37.5% natural abundance) and ^{187}Re (62.5% natural abundance). As a result, rhenium truxenyl complexes gave envelopes of parent ions. The calculated and observed parent ion patterns for Re_1(Tx), *trans*-Re_2(Tx) and *trans*-Re_3(Tx) match well confirming their stoichiometries (Table 3).

The trimetallic complexes were always the minor products as would be expected from steric factors when synthesized by Method A; or coulombic considerations



(4)

when synthesized by Method B were a trication is the synthetic intermediate. Collectively, 55% of truxene is functionalized with $Mn(CO)_3^+$ groups by Method A while 32% is complexed by Method B. The rhenium carbonyl complexes account for functionalizing 40% of the starting truxene. Solutions of either manganese or rhenium truxene complexes decomposed in ca. 30 min on exposure to air to truxene and an insoluble white precipitate. This behavior follows the trend of increasing reactivity of cyclopentadienyl < indenyl < fluorenyl metal complexes [17] where the truxenyl ligand structurally resembles the fluorenyl ligand.

The manganese and rhenium truxenyl complexes are thermally stable. The $Mn_1(Tx)$ and *trans*-$Mn_2(Tx)$ remained unchanged after heating to 60 °C for 4 h in THF-d_8 as observed by ^1H NMR in a sealed tube. The $Re_1(Tx)$ and *trans*-$Re_2(Tx)$ also remained unchanged under the same conditions.

Summary and conclusions

Truxenyl hydrocarbons with one, two or three manganese or rhenium tricarbonyl groups bound to the truxenyl five-membered rings were prepared. The manganese derivatives were prepared by two different synthetic routes; either by direct addition of the metal moieties to the Cp rings or by delivery to the Cp rings from the η^6-arene-coordinated intermediates through haptotropic rearrangements. The truxenyl *cis*-dimanganese complex was formed only through the arene-coordinated intermediates while the *trans* isomer was always obtained. These product distributions suggest that the truxenyl ligand forces *cis*-η^5-metal tricarbonyl groups close together to the extent that they are sterically crowded. Steric constraints of this type which are unique to these polynuclear systems will likely dictate product distributions in polymeric analogs as well. Different synthetic routes to otherwise similar products (i.e. Method A and B) could therefore be utilized to obtained organometallic polymers with a range of properties.

The externally fused arenes on truxenes greatly change the properties of "tris(Cp)" complexes when compared to our trindenyl metal complexes [18] which are both thermally robust and easily purified. The fused arenes provided a very attractive synthesis of a tris(Cp) ligand and allowed synthetic options for introducing metals into the tris(Cp) complexes, though their presence also led to enhanced air sensitivity and low solubility.

Experimental

General methods. Tetrahydrofuran, and hexane were distilled from benzophenone ketyl. 1,2-Dichloroethane and chloroform-d_1 were distilled from P_2O_5 and deoxygenated using three freeze-pump-thaw cycles. Truxene [8], $Mn(CO)_3(py)_2Br$ [19] and $[Re(CO)_3(THF)Br]_2$ [20] were prepared by literature methods. Silica gel for column chromatography was heated to 120 °C for 4 h prior to use. All reactions, manipulations and chromatography were performed under nitrogen using a combination of Schlenk techniques and a Vacuum Atmospheres glove box. Infrared spectra were recorded on a Perkin–Elmer 1800 FT-IR. NMR spectra were obtained on a General Electric QE-300 spectrometer. Mass spectra were obtained by the staff of the Mass Spectrometry Laboratory of the School of Chemical Sciences, University of Illinois-Urbana on a Varian-MAT 731 mass spectrometer.

Preparation of manganese truxene complexes

Method A. Truxene (115 mg, 0.336 mmol), potassium hydride (42 mg, 1.1 mmol) and ca. 2 mg KO-t-Bu were added to 50 ml of THF and stirred for 4 h. The compound $Mn(CO)_3(py)_2Br$ (382 mg, 1.01 mmol) was added and stirring was continued an additional 12 h followed by a 3 h reflux. An excess of NH_4Cl was added at room temperature followed by 2 h of stirring. The volume of the slurry was reduced to 10 ml and then was passed through a short silica gel column (2.5 cm dia. × 2.0 cm, 60–200 mesh) eluting with THF. Preparative thin layer chromatography (23 × 25 cm, 20 g silica gel, TLC grade; 18% THF/hexane eluant) gave four broad bands. The major components of the bands were as follows, in the order of decreasing mobility: (1) $Mn_1(Tx)$; (2) *trans*-$Mn_2(Tx)$; (3) *trans*-$Mn_2(Tx)$, $Mn_3(Tx)$; (4) $Mn_3(Tx)$. Yields are based on truxene and were calculated from the mass of the isolated TLC fractions in conjunction with integrations of the methine resonances in their ^1H NMR spectra: $Mn_1(Tx)$ (32 mg, 20%), *trans*-$Mn_2(Tx)$ (64 mg, 31%), *trans*-$Mn_3(Tx)$ (10 mg, 4%).

Method B. Truxene (77 mg, 0.23 mmol) and anhydrous aluminum chloride (138 mg, 1.04 mmol) were stirred in 20 ml of 1,2-dichloroethane for 10 min. The compound $Mn(CO)_5Br$ (233 mg, 0.850 mmol) was added and the mixture was refluxed for 15 h. Addition of 1,8-bis(dimethylamino)naphthalene (173 mg, 0.808 mmol) followed by 3 h of reflux gave a yellow-brown slurry. After removal of the solvent by vacuum, the residue was extracted into THF and passed through a short silica gel column and purified by preparative TLC as in Method A. Analysis of the four bands indicated there was one major component in each, giving yields of $Mn_1(Tx)$ (9 mg, 8%), *trans*-$Mn_2(Tx)$ (13 mg, 9%), *cis*-$Mn_2(Tx)$ (19 mg, 13%) and *trans*-$Mn_3(Tx)$ (4 mg, 2%).

Preparation of rhenium truxene complexes

Truxene (72 mg, 0.21 mmol), potassium hydride (29 mg, 0.72 mmol) $[Re(CO)_3(THF)Br]_2$ (288 mg, 0.341 mmol) and ca. 2 mg of KO-t-Bu were combined in 50 ml of THF and stirred for 24 h at ambient temperature. An excess of NH_4Cl was added to the mixture, then stirred for 2 h. The volume was reduced to 5 ml and the slurry was passed through a short silica gel column, eluting with THF. Removal of the solvent gave a yellow solid that was purified by preparative TLC (18% THF/hexane). Triple development [10] of the plate yielded significant purification of products. Two broad bands were collected. The most mobile band was enriched in $Re_1(Tx)$ while the major component of the second band was *trans*-$Re_2(Tx)$ along with a minor amount of *trans*-$Re_3(Tx)$. Yields were: $Re_1(Tx)$ (24 mg, 19%), *trans*-$Re_2(Tx)$ (32 mg, 17%) and *trans*-$Re_3(Tx)$ (10 mg, 4%).

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