Notes

Soft (S_3-Donor) Scorpionate Complexes of Molybdenum and Tungsten Carbonyls

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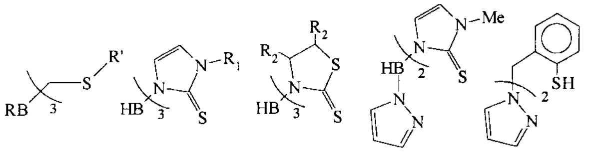
Summary: The dicarbonyl(η^3-allyl)molybdenum and tricarbonyliodotungsten complexes with hydrotris(methimazolyl)borate (Tm) are reported as the first examples of transition-metal organometallic complexes of the Tm ligand, serving as general entry points for a wide range of group 6 organometallic complexes. Their crystal structures have been determined, and comparisons are made with the homologous pyrazolylborate (Tp) and cyclopentadienyl (Cp) complexes, leading to predictions regarding their reactions.

Introduction

In recent years, a wide variety of soft, S_3 tripodal (scorpionate) ligands have been reported (Scheme 1).[1−6] Their relatively belated appearance in the literature is somewhat perplexing, considering that the reports thus far would suggest that the soft nature of these species does not compromise the ability of the ligand to form complexes. Our contribution has been the synthesis of the hydrotris(methimazolyl)borate anion (Tm)[2,3] and analogues derived from other thione-functionalized heterocycles.[4] As part of our formative studies we have endeavored to explore key areas of coordination/organometallic chemistry. Complexes derived from a wide variety of metals have been reported, from disparate areas of the periodic table (e.g. Li, Ru,[7] and Bi[8]) and significantly from every row of the transition metal series (Zn, Cd, Hg).[9] It would seem that these ligands have a potentially rich and important chemistry. A picture is emerging of facially capping six-electron-donor ligand systems with a synthetic utility comparable to the cyclopentadienyl (Cp) and poly(pyrazolyl) borate (Tp) anions. Consequently, throughout our studies we have sought to explore and exploit the soft nature of these ligands in direct comparison to Cp and Tp, particularly looking for subtle indications of graded changes in their structure and reactivity patterns.

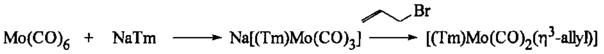
Scheme 1



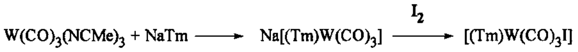
1 2(Tm) 3 4 5

R_1 = Me, Ph, Mes; R_2 = H, *o*-C_6H_4

Scheme 2



Scheme 3



To this end we have noted that [(Cp)Mo$(CO)_2$] fragments hold an important place in organometallic chemistry,[10,11] being particularly noted for their utility in organic synthesis (e.g., allylic substitutions).[12,13] Riordan has reported soft tris(alkylthiomethyl)borate complexes of a similar type,[1] prompting us to turn our attention to the organometallic compounds of the group 6 metals molybdenum and tungsten with our Tm ligand. While zinc and thallium methyl complexes of related ligands have been reported,[5] our studies have resulted in the first transition-metal organometallic complexes of the Tm ligand, which we report here, highlighting the possibilities offered by soft scorpionate ligands in this branch of chemistry.

Results and Discussion

The synthesis of the group 6 metal carbonyl complexes can be effected directly from the relevant metal carbonyl (Scheme 2) or from their tricarbonyl tris-

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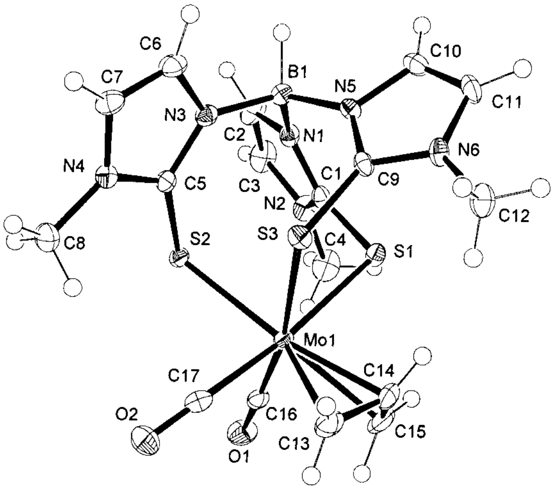

Figure 1. Structure of [(Tm)Mo(CO)$_2$(η^3-C$_3$H$_5$)] showing the atom-numbering scheme. Selected bond distances and angles are given in Table 1.

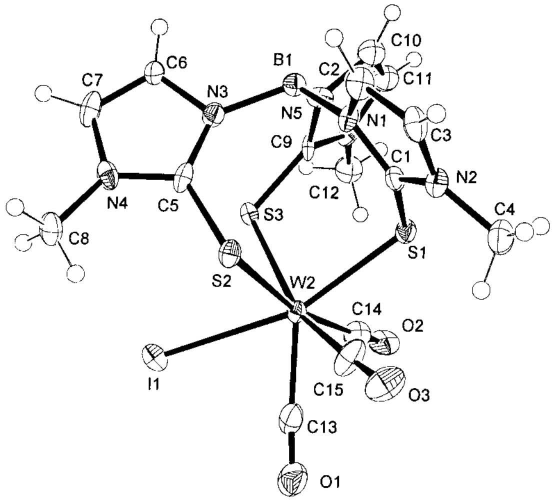

Figure 2. Structure of [(Tm)W(CO)$_3$I] showing the atom-numbering scheme. Selected bond distances and angles are given in Table 2.

(acetonitrile) complexes (Scheme 3). We have successfully employed both of these routes to prepare representative, key species for each metal, namely the η^3-allyl and the tricarbonyl iodide, obtaining each as reasonably air stable crystalline materials.

X-ray crystallography of the complexes [(Tm)Mo(CO$_3$)-(η^3-C$_3$H$_5$)] (Figure 1) and [(Tm)W(CO)$_3$I] (Figure 2) confirms in both cases the facial capping nature of the trithione ligand. In the molybdenum complex the metal−sulfur distances display a small extension for the sulfurs S(1) and S(3) trans to CO (2.641 Å) compared to the sulfur S(2) trans to the allyl group (2.559 Å), reflecting the relative trans effects of the CO and allyl ligands. The S−Mo−S angles (ligand bite angle) are unusually somewhat less than 90°, whereas in other known octahedral Tm complexes the corresponding angles are greater than 90°.[8,14,15] As a result, the twists of the heterocycle planes from the plane defined by the metal and the H−B−N unit are at the low end of the observed range (28.0−31.6°).

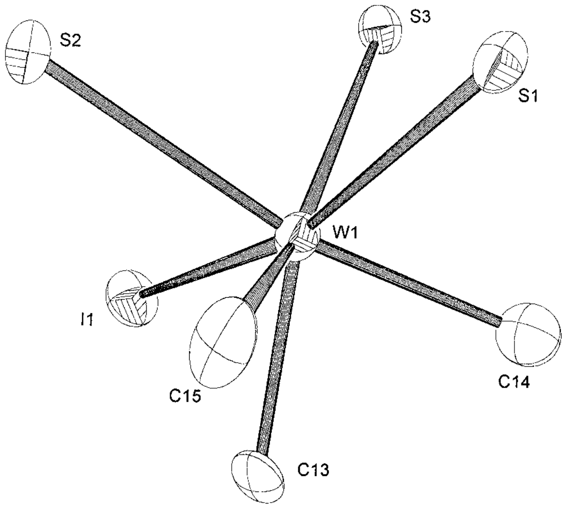

Figure 3. Tungsten coordination sphere in [(Tm)W(CO)$_3$I].

The tungsten coordination polyhedron in the seven-coordinate [(Tm)W(CO)$_3$I] (Figure 3) is best described as a capped octahedron, with atoms S(1), S(2), S(3), I(1), C(14), and C(15) defining the highly distorted octahedron. The carbonyl ligand associated with C(13) caps the I(1), C(14), C(15) face. The arrangement is very similar to that observed in the corresponding Tp$^{\mathrm{iPr}}$ complex,[16] but contrasts with the four-legged piano-stool (4:3) structure in the Cp[17] and macrocyclic thioether 9aneS$_3$[18] analogues. The structures are usually described in terms of distortions from idealized geometries, using the δ' angles defined by Muetterties and Guggenberger.[19] In this complex the angles are $\delta'_1 = 10.2°$, $\delta'_2 = 2.1°$, and $\delta'_3 = 19.5°$, compared to an idealized value of 16.2°. Key details of the coordination sphere are given in Table 2.

Despite there being two different types of methimazole rings (trans to CO, trans to allyl in the Mo complex and trans to I, trans to CO in the W complex), the ^{1}H NMR spectra show only one methimazole environment. The resonances are broad, suggesting that, as with the corresponding Tp compounds,[20] there is a degree of fluxionality in the complexes. This observation, coupled with the earlier report of Riordan,[1] indicates that the motif displayed by these soft tripodal ligands can be expected to be conserved in this area of organometallic chemistry.

The general similarity of the Mo(CO)$_2$(η^3-allyl) fragment to those found in the corresponding Cp and Tp complexes allows the influence of the facially capping ligand on the carbonyl and allyl ligands be explored in

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Table 1. Selected Structural and Spectroscopic Parameters for the Series of Compounds [(L)Mo(CO)$_2$(η^3-C$_3$H$_5$)] (L = Cp,[21,22] Tp,[20] Tm)

	CpMo	TpMo	TmMo
d(M−C)/Å	1.951	1.941	1.951
		1.950	1.950
d(C−O)/Å	1.156	1.155	1.157
		1.156	1.160
∠M−C−O/deg	178.9	176.1	175.7
		174.2	178.2
d(M−C$_t$)/Å	2.359	2.331	2.313
		2.349	2.341
d(M−C$_c$)/Å	2.236	2.227	2.220
∠C−C−C/deg	121.4	115.3	115.5
d(C$_t$−C$_c$)/Å	1.380	1.395	1.414
		1.400	1.340
ν(CO)/cm^{-1} (soln)	1963	1944	1927
	1889	1851	1835
δ(CO)/ppm	237.4	227.5	226.2

Table 2. Selected Bond Lengths (Å) and Angles (deg) for [(Tm)W(CO)$_3$I]

Bond Lengths			
W(1)−I(1)	2.9019(14)	W(1)−C(13)	1.98(2)
W(1)−S(1) (trans I)	2.528(4)	W(1)−C(14)	2.09(2)
W(1)−S(2) (trans CO)	2.573(4)	W(1)−C(15)	1.97(2)
W(1)−S(3) (trans CO)	2.597(4)		
Bond Angles			
S(1)−W(1)−S(2)	91.02(14)	C(14)−W(1)−S(1)	78.1(5)
S(1)−W(1)−S(3)	86.32(14)	C(15)−W(1)−S(2)	76.6(6)
S(2)−W(1)−S(3)	90.35(14)	C(13)−W(1)−S(2)	115.8(6)
S(1)−W(1)−I(1)	160.69(11)	C(14)−W(1)−S(2)	168.1(5)
S(2)−W(1)−I(1)	84.24(10)	C(15)−W(1)−S(3)	157.0(7)
S(3)−W(1)−I(1)	75.03(10)	C(13) −W(1)−S(3)	132.3(6)
C(15)−W(1)−C(13)	70.7(9)	C(14)−W(1)−S(3)	84.4(5)
C(15)−W(1)−C(14)	104.6(8)	C(15)−W(1)−I(1)	121.4(7)
C(13)−W(1)−C(14)	75.3(7)	C(13)−W(1)−I(1)	69.3(6)
C(15)−W(1)−S(1)	75.2(7)	C(14)−W(1)−I(1)	104.6(5)
C(13)−W(1)−S(1)	129.0(6)		

detail. The most obvious probe of the subtle effects of the different face-capping ligands is in the carbonyl groups (Table 1). The structural data do not indicate significant alteration in the M−C and C−O bond distances in the solid state. Despite this, marked variations are apparent in the infrared spectra, where the ν(CO) value can be seen to move to lower frequency along the series Cp → Tp → Tm, indicative of a progressive change in donor properties of the facial ligand. Cp is able to act as a π-acceptor and competes with CO for electron density, resulting in the higher ν(CO) value. The Tp and Tm complexes have successively lower values, suggesting progressively greater electron density at the metal. This is commensurate with Tp acting as a strong σ-donor with little or no π-interaction from the heterocycle π-system, while the lone pairs on the sulfur donors of Tm will overlap efficiently with the metal orbitals, giving strong π-donation. This situation is also reflected in the observed positions of the carbonyls in the ^{13}C NMR spectra. A similar trend in ν(CO) is also observed for the corresponding tungsten complexes, [(L)W(CO)$_3$I] (Table 3).

Table 3. Carbonyl Stretching Bands, ν(CO), for the Series of Compounds [(L)W(CO)$_3$I] (L = Tp,[23] Cp,[24] Tm)

ν(CO)/cm^{-1}		
CpW(CO)$_3$I	TpW(CO)$_3$I	TmW(CO)$_3$I
2030	2021	2004
1944	1942	1916
1936	1904	1902

The utility of these species rests in their ability to control and effect changes in the ancillary ligands. Thus, a comparative analysis of the η^3-allyl fragments for the three capping ligands (Table 1) is of major interest. Here again subtle changes are found in the relationship of the allylic ligand to its metal. In each case the allyl group adopts an exo conformation with respect to the M(CO)$_2$ fragment. However, the M−C$_c$ (2.236, 2.227, 2.220 Å) and M−C$_t$ (2.359, 2.340 (av), 2.327 (av) Å) distances decrease slightly along the series Cp, Tp, Tm, suggesting a progressively tighter binding of the allyl fragment, which may possibly convert into a greater reactivity toward substitution. A further difference is seen in the Tm system, which has a substantially asymmetric allyl ligand (d(C−C) = 1.340, 1.414 Å) in contrast to the symmetrical arrangement in the Cp and Tp complexes. Curiously, the C$_t$−C$_c$−C$_t$ angles are identical for the Tm and Tp complexes but some 6° larger for the Cp complex.

Altering the nature of the facially capping ligand has introduced a subtle reorganization in the ancillary ligand. Should similar effects be repeated in the presence of synthetically valuable organic fragments, it should be possible to alter the reaction profile, particularly with respect to the stereo- and regiochemistry of allylic substitution. It is noteworthy that the methyl group, C(12), on the methimazole ring most closely associated with the allyl group projects toward the central carbon of the allyl fragment. Furthermore, as a result of the ligand twist there is an asymmetry to the interaction. It is expected that this interaction will affect the orientation of complexation of substituted allyl fragments, influencing in turn the stereochemistry of their reactions. This interaction could be further tuned by replacing methyl with more bulky groups.

Experimental Section

All reactions were carried out under an atmosphere of dry N$_2$, in dried, freshly distilled solvents. NaTm[3] and [W(CO)$_3$(NCMe)$_3$][25] were prepared by literature methods. All other reagents were purchased and used as received. NMR spectra were were recorded on a Bruker AMX400 spectrometer and are referenced to internal solvent peaks.

Preparation of [(Tm)Mo(CO)$_2$(η^3-allyl)]. Mo(CO)$_6$ (0.247 g, 0.94 mmol) and NaTm (0.354 g, 0.95 mmol) were refluxed together in tetrahydrofuran (75 mL) for 6 h. The solution was cooled and treated with allyl bromide (0.140 g, 1.15 mmol), whereupon a greenish solid was formed. The mixture was refluxed for a further 15 min and the solid redissolved. Filtration through a pad of alumina, concentration, and addition of hexane resulted in a yellow-brown solid (yield 0.20 g, 40%). Crystals suitable for X-ray diffraction were obtained by slow diffusion of hexane into a solution of the complex in THF. Anal. Found: C, 38.13; H, 4.07; N, 14.87; S, 16.99. Calcd for C$_{17}$H$_{21}$N$_6$S$_3$O$_2$BMo·0.1C$_6$H$_{14}$: C, 38.22; H, 4.08; N, 15.20; S, 17.39. ^{1}H NMR (400 MHz, CDCl$_3$): δ 1.20 (dd, 2H, CH$_2$), 3.28 (m, 2H, CH$_2$), 3.65 (m, 1H, CH), 3.68 (s, 9H, CH$_3$), 6.74

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Table 4. Crystallographic Information

	[(Tm)Mo(CO)$_2$(η^3-allyl)]	[(Tm)W(CO)$_3$I]
formula	$C_{17}H_{21}BMoN_6O_2S_3$	$C_{15}H_{16}BIN_6O_3S_3W\cdot C_4H_{10}O$
fw	544.33	868.08
cryst syst	monoclinic	monoclinic
space group	*C*2/*c* (No. 15)	*P*2$_1$/*n* (No. 14)
a/Å	28.8124(7)	12.8780(2)
b/Å	13.3494(4)	15.3477(3)
c/Å	12.7461(4)	14.0110(3)
α/deg	90	90
β/deg	115.962(1)	94.975(1)
γ/deg	90	90
V/Å^3	4407.8(2)	2758.81(9)
Z	8	4
D_{calcd}/g cm^{-3}	1.641	1.975
F(000)	2208	1576
μ/mm^{-1}	0.906	5.57
2θ range/deg	6.86−54.62	6.88−54.56
no. of rflns measd	8463	24976
no. of unique rflns	4878	6168
R_{merge}	0.034	0.094
R1, wR2	0.033, 0.062	0.081, 0.23
GOF	1.057	1.16

(d, 3H, CH), 6.79 (d, 3H, CH). IR (CH_2Cl_2 solution): ν(B−H) 2444 cm^{-1}, ν(CO) 1927, 1835 cm^{-1}.

Preparation of [(Tm)W(CO)$_3$I]. W(CO)$_3$(NCMe)$_3$ (0.660 g, 1.69 mmol) and NaTm (0.632 g, 1.69 mmol) were stirred at room temperature in CH_2Cl_2 (40 mL) for 3 days to give a red solution, which was treated with I_2 (0.229 g, 0.90 mmol), and the solution was stirred for a further 1 day. The resulting deep red solution was filtered through Celite, the solvent was evaporated in vacuo, and the solid was washed with three portions of diethyl ether to remove any residual iodine. The residue was redissolved in CH_2Cl_2 and the product precipitated with hexane. The red solid was collected by filtration, washed with hexane, and vacuum-dried (yield 0.403 g, 30%). Crystals for X-ray diffraction were grown by slow diffusion of diethyl ether into a CH_2Cl_2 solution. Anal. Found: C, 18.28; H, 2.10; N, 9.08. Calcd for $C_{15}H_{16}N_6S_3O_3BWI\cdot 2CH_2Cl_2$: C, 22.29; H, 2.20; N, 9.18. Consistently low % C values were obtained for this complex, which we believe to be due to carbide formation. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.81 (s, 3H, CH_3), 6.90 (s, 1H, CH), 6.94 (s, 1H, CH). IR: ν(CO) 2004, 1916, 1902 cm^{-1}.

X-ray Crystallography. Crystallographic data for the complexes [(Tm)Mo(CO$_3$)(η^3-C_3H_5)] and [(Tm)W(CO)$_3$I] are given in Table 4. Data were collected on a Nonius Kappa-CCD diffractometer using graphite-monochromated Mo Kα radiation (0.710 73 Å). The structures were solved using Patterson methods (SHELXS-86),[26] expanded by Fourier synthesis, and refined by full-matrix least squares on F^2 (SHELXL-93).[27] Non-hydrogen atoms were refined anisotropically and hydrogen atoms placed in calculated positions, riding on the parent atom. The structure of [(Tm)W(CO)$_3$I] was slightly problematic, in that we were unable to apply a meaningful absorption correction. The consequence is that, while the atom positions and identities are unambiguous, residual electron density in the vicinity of the tungsten atom was on the order of 6 e Å^{-3}, while the residuals and esd's on the metrical parameters were slightly higher than normal. All calculations used the WinGX graphical interface.[28] The crystallographic data for both compounds have been deposited at the Cambridge Crystallographic Data Centre as Supplementary Publication Nos. CCDC-169207 and CCDC-169208. Copies of the data can be obtained free of charge on application to: CCDC, 12 Union Road, Cambridge, U.K. CB2 1EZ (fax, +44 1223 336033; e-mail, deposit@ccdc.cam.ac.uk).

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Supporting Information Available: Crystallographic data in CIF format for both reported structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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