Inorg. Chem. **2000,** *39,* 1561−1567

Syntheses and Structures of Methyltris(pyrazolyl)silane Complexes of the Group 6 Metals

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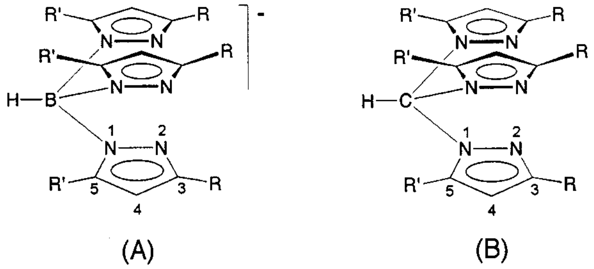
Received August 6, 1999

The methyltris(3,5-dimethylpyrazolyl)silane ligand, Tps^{Me_2}, was readily prepared by the metathesis reaction of methyltrichlorosilane with 3 equiv of lithium 3,5-dimethylpyrazolate. The octahedral tricarbonyl complexes $(\text{Tps}^{\text{Me}_2})\text{M(CO)}_3$ were synthesized either by ligand exchange with the labile nitrile adducts $\text{M(CO)}_3\text{(NCR)}_3$ (M = Cr, Mo, R = Me; M = W, R = Et) or thermally by direct substitution on the hexacarbonyls M(CO)_6 (M = Cr, Mo). The three new complexes were characterized by a combination of analytical and spectroscopic techniques, including electrospray ionization mass spectrometry and single-crystal X-ray diffraction. They are all isostructural and display in the solid state the expected distorted octahedral geometries with facially coordinated tris(pyrazolyl)silane ligands. Crystallographic data were used to calculate the ligand cone angles (251−264°) in $(\text{Tps}^{\text{Me}_2})\text{M(CO)}_3$ and also to estimate a value of 1.59 Å for the covalent radius of octahedral W(0).

Introduction

Since their genesis in the mid 1960s,[1,2] the tris(pyrazolyl)borates (Chart 1A) have established themselves as some of the most useful ligands in modern coordination chemistry.[3] Their versatility is derived from the different steric and electronic effects that can be attained by varying the nature, number, and position of the substituents in the pyrazole rings in order to fine-tune the reactivity at the metal centers. Not surprisingly, these multifarious ligands have been used to prepare complexes with virtually every metal in the periodic table, having applications from homogeneous catalysis to bioinorganic chemistry.[4−6] In contrast, the coordination chemistry of their neutral, isosteric, and isoelectronic carbon-centered analogues, the tris(pyrazolyl)methanes (Chart 1B), is noticeably underdeveloped.[7−10] In fact, most of the studies of these tridentate ligands since Trofimenko's seminal paper on poly(pyrazolyl)alkanes[11] are circumscribed to the unsubstituted ligand HC(pz)_3 and, to a lesser degree, the 3,5-dimethylpyrazolyl homologue $\text{HC(3,5-Me}_2\text{pz)}_3$.[12−38] While rapid progress in tris(pyrazolyl)methane coordination chemistry may have initially been hampered by the modest yields in which $\text{HC(3,5-R}_2\text{pz)}_3$ (R = H, Me) were available (vide infra),[11,39]

Chart 1. $[\text{HB(3,5-RR}'\text{pz)}_3]^-$ ("Tp") and $\text{HC(3,5-RR}'\text{pz)}_3$ Ligands



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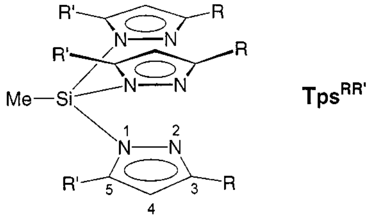
10.1021/ic990945l CCC: $19.00

Chart 2. MeSi(3,5-RR′pz)$_3$ (“Tps”) Ligands



this factor alone does not explain the slow evolution of their chemistry, especially if compared with that of the tris(pyrazolyl)borates. It is also noteworthy that the first structurally characterized transition metal complexes incorporating HC(3,5-Me$_2$pz)$_3$, some molybdenum derivatives including $\{\eta^3$-HC(3,5-Me$_2$pz)$_3\}$-MoI$_3$, were only reported in 1995.[40] More recently, in an effort to investigate tris(pyrazolyl)methane ligands analogous to the so-called “tetrahedral enforcer” tris(pyrazolyl)borates,[41] Vahrenkamp[42] and Reger[43-45] have independently synthesized derivatives bearing bulkier substituents (e.g., Pr^i, Bu^t, Ph) in the 3-position of the pyrazolyl rings. However, these sterically demanding ligands are also typically obtained only in moderate yields (25−55%) and their isolation in pure form requires several purification steps (e.g., extractions and neutralizations, column chromatography, recrystallizations).[46,47]

Motivated by the practical shortcomings that affect the reported syntheses of the tris(pyrazolyl)methanes, we set out to develop the chemistry of the tris(pyrazolyl)silane ligands (Chart 2) as alternative neutral analogues of the tris(pyrazolyl)borates. Additionally, we were also interested in evaluating the effect on the ligand’s flexibility (i.e., cone angles) of the larger silicon atoms in the tris(pyrazolyl)silanes relative to the carbon centers in the tris(pyrazolyl)methanes. On the basis of nomenclature proposed for the tris(pyrazolyl)borates,[3] we will abbreviate the new ligands Tps$^{RR'}$, where R and R′ are the alkyl and aryl substituents in the 3- and 5-positions of the pyrazolyl rings, respectively, and a methyl group is assumed to be attached to the silicon center. To our surprise, the only literature references to poly(pyrazolyl)silanes, other than the unpublished work of F. Klanberg,[48] appear to be the X-ray structure of methyltris(3,5-dimethylpyrazolyl)silane, Tps^{Me_2},[49] and our recent preliminary report on the syntheses of Tps^{Me_2}, Tps$^{Bu^t}$, and their copper(I) complexes [LCu(NCMe)]PF$_6$.[50] We present herein a detailed account on the preparation and characterization of Tps^{Me_2} and the syntheses and structures of its group 6 metal carbonyl derivatives (Tps^{Me_2})M(CO)$_3$ (M = Cr, Mo, W).

Results and Discussion

Ligand Synthesis. Tps^{Me_2} was first prepared by the transsilylation reaction of methyltrichlorosilane and (3,5-dimethylpyrazolyl)trimethylsilane:[49]

$$\mathrm{MeSiCl_3 + 3Me_3Si(3{,}5\text{-}Me_2pz)} \xrightarrow[-3\mathrm{MeCl}]{} \mathrm{Tps^{Me_2}} \qquad (1)$$

Although neither the yield for the reaction nor spectroscopic data for the product were reported, it was characterized unequivocally by single-crystal X-ray diffraction. As an alternative approach for producing tris(pyrazolyl)silanes, we considered that simple metathesis reactions between alkyltrichlorosilanes and alkali metal pyrazolates,

$$\mathrm{RSiCl_3 + 3M(pz)} \xrightarrow[\mathrm{M = Li,\,Na,\,K}]{} \mathrm{RSi(pz)_3 + 3MCl} \qquad (2)$$

would lead to the desired products. In this regard, we note that poly(pyrazolyl)methanes H$_n$C(pz)$_{4-n}$ (n = 0, 1, 2) have been similarly prepared by reacting halomethanes (e.g., CCl$_4$, CHCl$_3$, CH$_2$I$_2$) with sodium or potassium pyrazolates, although yields are particularly disappointing for the tertiary and quaternary derivatives [e.g., 34% for HC(pz)$_3$, 17% for HC(3,5-Me$_2$pz)$_3$].[11,39] While improved yields have been obtained using phase-transfer catalysis protocols [up to 62% for HC(pz)$_3$, 30% for HC(3,5-Me$_2$pz)$_3$, and 63% for the trimethylpyrazolyl derivative HC(3,4,5-Me$_3$pz)$_3$],[51,52] we envisioned that the enhanced reactivity of the Si−Cl bonds in RSiCl$_3$, relative to that of the C−Cl bonds in CHCl$_3$, should result in the formation of tris(pyrazolyl)silanes in even better yields. Indeed, we found that the silane Tps^{Me_2} can be easily synthesized by reacting MeSiCl$_3$ with 3 equiv of lithium 3,5-dimethylpyrazolate in pentane:

$$\mathrm{MeSiCl_3 + 3Li(3{,}5\text{-}Me_2pz)} \xrightarrow[-3\mathrm{LiCl}]{\text{pentane}} \mathrm{Tps^{Me_2}} \qquad (3)$$

The product is isolated as an analytically pure white solid in almost quantitative yield (90−95%) by evaporating to dryness the solution obtained after separating by filtration the generated LiCl. Tps^{Me_2} is stable in dry air for at least 2 years, and it is soluble in a variety of common organic solvents, including aliphatic and aromatic hydrocarbons, ethers, dichloromethane, and acetonitrile. Nonetheless, it slowly decomposes in the presence of water or alcohols, an important difference with the tris(pyrazolyl)methanes.

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Group 6 Metal Carbonyl Complexes. The yellow tricarbonyl complexes $(\mathrm{Tps}^{\mathrm{Me}_2})\mathrm{M(CO)}_3$ (M = Cr, Mo, W) were readily prepared in 60−75% yield from the reactions of equimolar amounts of the labile nitrile adducts $\mathrm{M(CO)_3(NCMe)_3}$ (M = Cr, Mo) or $\mathrm{W(CO)_3(NCEt)_3}$ and the silane ligand in acetonitrile or tetrahydrofuran:

$$\mathrm{M(CO)_3(NCR)_3} + \mathrm{Tps}^{\mathrm{Me}_2} \xrightarrow[-3\mathrm{RCN}]{\mathrm{MeCN}} (\mathrm{Tps}^{\mathrm{Me}_2})\mathrm{M(CO)_3} \quad (4)$$

The three tris(pyrazolyl)silane complexes are diamagnetic, moderately air-sensitive solids, only slightly soluble in polar coordinating solvents such as acetonitrile. The chromium and molybdenum compounds can also be synthesized directly from the hexacarbonyls $\mathrm{M(CO)_6}$ in refluxing methylcyclohexane, but only the latter was obtained in good yield (71%).

Characterization of $(\mathrm{Tps}^{\mathrm{Me}_2})\mathrm{M(CO)_3}$. The new complexes were characterized by a combination of analytical and spectroscopic techniques including elemental analysis, ^{1}H NMR, ^{13}C NMR, and IR spectroscopies, mass spectrometry, and X-ray crystallography. Spectroscopic data in solution are consistent with the presence of tridentate (η^3-) facially coordinated silane ligands in the $(\mathrm{Tps}^{\mathrm{Me}_2})\mathrm{M(CO)_3}$ complexes, all of which show magnetically equivalent pyrazolyl groups on the NMR time scale. Whereas the methyl substituents in the pyrazolyl rings appear in the ^{1}H NMR spectra (obtained in $\mathrm{CD_3CN}$) between 2.4 and 2.7 ppm, shifted ca. 0.5−0.8 ppm downfield relative to the free ligand, the chemical shifts of the other protons are less affected (MeSi−) or remain virtually unchanged (4-*H*) upon coordination. Similarly, modest downfield shifts of between 1.3 and 5.1 ppm ppm relative to the free ligand are found for all the carbon signals in the $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR spectra of the $\mathrm{Tps}^{\mathrm{Me}_2}$ complexes, with the carbonyl groups being characterized by chemical shifts of 234.3, 228.8, and 223.4 ppm for M = Cr, Mo, and W, respectively. While no such data have apparently been reported for any of the related group 6 complexes $[(\mathrm{Tp})\mathrm{M(CO)_3}]^-$ or $\{\mathrm{HC(3,5\text{-}R_2pz)_3}\}\mathrm{M(CO)_3}$, these chemical shifts are nevertheless typical of terminal CO ligands.[53] In addition, chemical shifts of 206.9 and 221.9 ppm have been reported for the (presumably) trans and cis carbonyl groups in the related bis(3,5-dimethylpyrazolyl)methane complex *cis*-$\{\mathrm{H_2C(3,5\text{-}Me_2pz)_2}\}\mathrm{Mo(CO)_4}$.[54] Furthermore, the aforementioned values reflect the increase in shielding of the carbonyl carbon nucleus with increasing atomic number, a general trend observed for a given group of transition metal carbonyl compounds.[55]

The $(\mathrm{Tps}^{\mathrm{Me}_2})\mathrm{M(CO)_3}$ complexes were also characterized in the solid state by IR spectroscopy. The spectrum of each compound, obtained as a KBr pellet, shows two strong absorptions in the carbonyl region, at ca. 1895 cm^{-1} (A_1 mode) and 1750 cm^{-1} (E mode), as expected for the facial isomer of an octahedral tricarbonyl complex.[56] The observed ν(CO) values are all comparable to those reported for related tris(pyrazolyl)methane and tris(pyrazolyl)borate tricarbonyl group 6 metal complexes (Table 1), an observation that underscores the isoelectronic nature of the three ligand systems.

Electrospray ionization mass spectrometry (ESI-MS)[57−60] was applied to further characterize the $(\mathrm{Tps}^{\mathrm{Me}_2})\mathrm{M(CO)_3}$ compounds. By use of dilute acetonitrile solutions of the complexes, peaks with the expected isotopic distribution were observed in the mass spectra at m/z = 464, 510, and 595 (for M = Cr, Mo, and W, respectively) and assigned to the corresponding molecular ions. Interestingly, intense signals for the corresponding $[\mathrm{M} - 3\mathrm{CO}]^+$ fragments, rather than for the $[\mathrm{M} - \mathrm{Tps}^{\mathrm{Me}_2}]^+$ groups, were present. In addition, the spectra of the three complexes exhibit peak clusters centered at m/z = 935, 1023, and 1193 (for M = Cr, Mo, and W, respectively), suggesting the presence of dimeric noncovalent aggregates, a phenomenon not uncommon in ESI-MS.

Table 1. IR Data for $(\mathrm{Tps}^{\mathrm{Me}_2})\mathrm{M(CO)_3}$ (M = Cr, Mo, W) and Related Complexes

complex	ν(CO)/cm^{-1}	reference
$(\mathrm{Et_4N})[(\mathrm{Tp}^{\mathrm{Me}_2})\mathrm{Cr(CO)_3}]$	1891, 1748[a]	*b*
$\{\mathrm{HC(pz)_3}\}\mathrm{Cr(CO)_3}$	1898, 1758[c]	*d*, *e*
$(\mathrm{Tps}^{\mathrm{Me}_2})\mathrm{Cr(CO)_3}$	1898, 1755[f]	this work
$(\mathrm{Et_4N})[(\mathrm{Tp})\mathrm{Mo(CO)_3}]$	1897, 1761[a]	*b*, *g*
$(\mathrm{NCP})[(\mathrm{Tp})\mathrm{Mo(CO)_3}]$[h]	1882, 1736[f]	*i*
$(\mathrm{Et_4N})[(\mathrm{Tp}^{\mathrm{Me}})\mathrm{Mo(CO)_3}]$	1892, 1753[a]	*j*
$(\mathrm{Et_4N})[(\mathrm{Tp}^{\mathrm{Me}_2})\mathrm{Mo(CO)_3}]$	1891, 1751[a]	*b*
$(\mathrm{Bu}^n{}_4\mathrm{N})[(\mathrm{Tp}^{\mathrm{Me}_2})\mathrm{Mo(CO)_3}]$	1886, 1749[a,k]	*l*
$\{\mathrm{HC(pz)_3}\}\mathrm{Mo(CO)_3}$	1882, 1765[c]	*d*
$\{\mathrm{HC(3,5\text{-}Me_2pz)_3}\}\mathrm{Mo(CO)_3}$	1900, 1760[c]	*d*, *m*
$(\mathrm{Tps}^{\mathrm{Me}_2})\mathrm{Mo(CO)_3}$	1896, 1755[f]	this work
$(\mathrm{Et_4N})[(\mathrm{Tp}^{\mathrm{Me}_2})\mathrm{W(CO)_3}]$	1881, 1744[a]	*b*
$\{\mathrm{HC(pz)_3}\}\mathrm{W(CO)_3}$	1886, 1759[c]	*d*
$(\mathrm{Tps}^{\mathrm{Me}_2})\mathrm{W(CO)_3}$	1887, 1747[f]	this work

[a] Acetonitrile solution. [b] Trofimenko, S. *J. Am. Chem. Soc.* **1969**, *91*, 588−595. [c] Nujol mull. [d] Trofimenko, S. *J. Am. Chem. Soc.* **1970**, *92*, 5118−5126. [e] Values of 1900 and 1765 cm^{-1} (Nujol mull) have also been reported. Armanasco, N. L.; Baker, M. V.; North, M. R.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1997**, 1363−1368. [f] KBr pellet. [g] Values of 1890 and 1750 cm^{-1} (KBr pellet) have also been found. Curtis, M. D.; Shiu, K.-B. *Inorg. Chem.* **1985**, *24*, 1213−1218. [h] NCP = *N*-methyl-4-cyanopyridinium, *p*-$\mathrm{NCC_5H_4NMe^+}$. [i] Bockman, T. M.; Kochi, J. K. *New J. Chem.* **1992**, *16*, 39−49. [j] Desmond, T. J.; Lalor, F. J.; Ferguson, G.; Parvez, M. *J. Organomet. Chem.* **1984**, *277*, 91−97. [k] Values of 1882 and 1728 cm^{-1} (KBr pellet), 1883 and 1743 cm^{-1} ($\mathrm{CH_2Cl_2}$), and 1878 and 1738 cm^{-1} (toluene) were also reported. [l] Protasiewicz, J. D.; Theopold, K. H. *J. Am. Chem. Soc.* **1993**, *115*, 5559−5569. [m] Values of 1900 and 1763 cm^{-1} (KBr pellet) have also been observed. Dhawan, I. K.; Bruck, M. A.; Schilling, B.; Grittini, C.; Enemark, J. H. *Inorg. Chem.* **1995**, *34*, 3801−3808.

Structures of $(\mathrm{Tps}^{\mathrm{Me}_2})\mathrm{M(CO)_3}$ (M = Cr, Mo, W). The molecular structures of the isostructural $(\mathrm{Tps}^{\mathrm{Me}_2})\mathrm{M(CO)_3}$ complexes (M = Cr, Mo, W) have been determined by single-crystal X-ray diffraction, with that of the chromium compound shown in Figure 1, and a selection of bond lengths and angles are given in Table 2. It is noteworthy that this is the first complete series of group 6 metal tricarbonyl complexes $\mathrm{LM(CO)_3}$ to be structurally characterized for L = tris(pyrazolyl)borate, -methane, or -silane ligands. While the three compounds are isostructural, packing differences result in the chromium compound crystallizing in the monoclinic space group $P2_1/m$ (no. 11) with two molecules in the unit cell and the isomorphous Mo and W analogues crystallizing in the orthorhombic space group *Pnma* (no. 62) with four molecules per unit cell. In both cases the molecules lie on crystallographic mirror planes containing one of the pyrazole rings, the silicon and metal atoms, and a carbonyl

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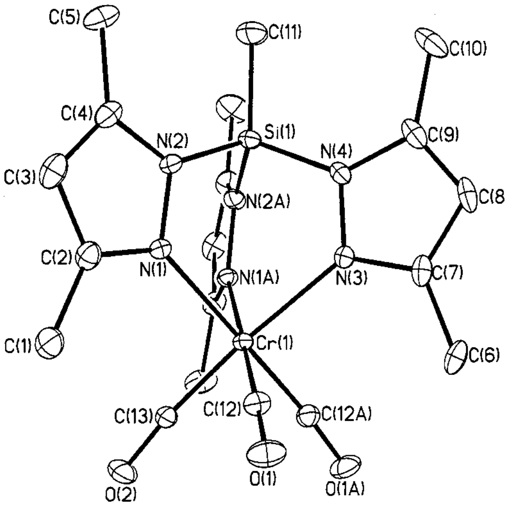

Figure 1. ORTEP diagram of $(\text{Tps}^{\text{Me}_2})\text{Cr(CO)}_3$ with thermal ellipsoids at the 30% probability level and hydrogen atoms omitted for clarity.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for the $(\text{Tps}^{\text{Me}_2})\text{M(CO)}_3$ Complexes

	M = Cr	M = Mo	M = W
M−N(1)	2.164(3)	2.318(3)	2.288(4)
M−N(3)	2.182(4)	2.297(4)	2.280(5)
M−C(12)	1.817(4)	1.944(3)	1.941(5)
M−C(13)	1.813(5)	1.938(5)	1.942(6)
C(12)−O(1)	1.172(5)	1.179(4)	1.181(6)
C(13)−O(2)	1.173(7)	1.181(6)	1.181(8)

	M = Cr	M = Mo	M = W
C(12)−M−C(12A)	84.7(3)	85.2(2)	85.5(3)
C(12)−M−C(13)	83.47(17)	80.38(14)	81.00(19)
C(12)−M−N(1)	95.45(16)	95.77(13)	95.69(18)
C(12)−M−N(1A)	179.46(15)	178.72(12)	178.62(17)
C(12)−M−N(3)	93.13(14)	96.06(13)	96.14(17)
C(13)−M−N(1)	96.03(14)	100.55(12)	99.82(17)
C(13)−M−N(3)	175.38(19)	175.12(17)	176.1(2)
N(1)−M−N(1A)	84.38(16)	83.21(15)	83.1(2)
N(1)−M−N(3)	87.39(11)	83.07(10)	83.08(13)
M−C(12)−O(1)	174.5(3)	174.4(3)	175.5(4)
M−C(13)−O(2)	172.3(5)	170.2(4)	171.3(5)

group. Overall, the three structures resemble those of the anionic tris(pyrazolyl)borate complexes $[(\text{Tp})\text{Mo(CO)}_3]^-$,[61] $[(\text{Tp}^{\text{Me}})\text{Mo(CO)}_3]^-$,[62] and $[(\text{Tp}^{\text{Me}_2})\text{Mo(CO)}_3]^-$ [63,64] and also those of the 17-electron radicals TpMo(CO)_3 [65] and $(\text{Tp}^{\text{Me}_2})\text{Mo(CO)}_3$.[66] Interestingly, no chromium or tungsten tricarbonyl complexes containing tris(pyrazolyl)-type ligands have apparently been structurally characterized prior to our work, although the closest relative could be the neutral paramagnetic tetrakis(pyrazolyl)borate complex $(\text{pzTp})\text{Cr(CO)}_3$.[67]

The six-coordinate complexes display in the solid state the expected distorted octahedral geometries, with tridentate face-capping tris(pyrazolyl)silane ligands. The three M−CO moieties in each complex are roughly opposite to the three M−N bonds, with the average $\text{N}-\text{M}-\text{C}_{\text{trans}}$ angle being ca. 178°. The silicon centers in each derivative are approximately tetrahedral, with mean N−Si−N and C−Si−N angles of 106.3 and 112.3°, values that are remarkably close to those found for the free Tps^{Me_2} ligand (107.5 and 111.3°, respectively).[49] The observed N−Si−N angles in $(\text{Tps}^{\text{Me}_2})\text{M(CO)}_3$ are somewhat smaller than the N−C−N angles (in the range 109−114°) found in $\text{HC(3,5-Me}_2\text{pz)}_3$[68] and its coordination complexes.[17−20,40,44,45] Conversely, the C−Si−N angles in Tps^{Me_2} are moderately larger than the corresponding H−C−N angles in $\text{HC(3,5-Me}_2\text{pz)}_3$ (ca. 108°). These observations suggest that the Tps^{Me_2} ligand may actually have a slightly smaller "bite" angle than $\text{HC(3,5-Me}_2\text{pz)}_3$ despite the larger covalent radius of Si vs C (1.17 and 0.77 Å, respectively).[69] It is likely that the presence of the methyl group bound to silicon in Tps^{Me_2}, in contrast to the hydrogen atom attached to the carbon or boron atoms in tris(pyrazolyl)methanes and -borates, is responsible for this situation. More importantly, ligand cone angles of 264, 258, and 251° have been calculated from the X-ray data for $(\text{Tps}^{\text{Me}_2})\text{M(CO)}_3$ (M = Cr, Mo, W, respectively).[70] These values are not only 20−30° larger than those observed in Tp^{Me_2} complexes but also unexpectedly approach those estimated for bulkier ligands such as Tp^{Bu^t} (265°),[71] for which six-coordination is relatively rare.[4,5]

The average Mo−N bond distance (2.311 Å) in $(\text{Tps}^{\text{Me}_2})\text{Mo(CO)}_3$ is only marginally longer (ca. 0.04 Å) than the corresponding values found in the few known molybdenum tris(pyrazolyl)borate tricarbonyl complexes.[61−64] While there are no structurally characterized Tp analogues of $(\text{Tps}^{\text{Me}_2})\text{M(CO)}_3$ (M = Cr, W), the M−N bond lengths in all three species are comparable to the corresponding values reported for other neutral zerovalent tricarbonyl complexes $\text{L}_3\text{M(CO)}_3$ (L = nitrogen donor ligand) of chromium (2.17−2.21 Å),[72,73] molybdenum (2.24−2.41 Å),[74−81] and tungsten (2.20−2.33 Å).[74,75,82] In addition, assuming a covalent radius of 0.70 Å for nitrogen[69] and by adoption of the covalent radii for octahedral Cr(0) and Mo(0) estimated by Cotton,[72] the calculated Cr−N and Mo−N single bond lengths are 2.18 and 2.32 Å, values that are virtually identical to those observed for $(\text{Tps}^{\text{Me}_2})\text{M(CO)}_3$ (M = Cr, Mo). Encouraged by these results but acknowledging that the covalent

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radius of tungsten is particularly ill-defined,[83] we can similarly derive a value of 1.59 Å for the covalent radius of W(0) in an octahedral environment on the basis of the average W−N distance (2.29 Å) found in (Tps^{Me_2})W(CO)$_3$. It is interesting to note that values of 1.57 and 1.58 Å have been estimated before for r_{cov}(W) based on the X-ray structure analysis of CpW(CO)$_3$Ph.[84]

The average M−C bond lengths in (Tps^{Me_2})M(CO)$_3$ (1.816, 1.942, and 1.941 Å for M = Cr, Mo, W, respectively) are typical, and so are the mean C−O bond distances (ca. 1.18 Å) and the fairly linear M−C−O angles (ca. 173°).[85] All the other interatomic bond lengths (i.e., C−N, N−N, Si−C, and Si−N) also seem to be normal.[86] It is also worth mentioning that both the M−N and M−C distances are slightly shorter for molybdenum than for tungsten, an observation that is yet another example of the significant effect of the lanthanide contraction in the size of the elements following the lanthanides in the periodic table.[87]

Conclusions

In contrast to the reported syntheses of tris(pyrazolyl)methanes, the reaction between methyltrichlorosilane and a lithium pyrazolate proved to be a straightforward approach for synthesizing in excellent yield functionalized silanes such as Tps^{Me_2}. We have also extended this methodology to prepare the related bis(pyrazolyl)dimethylsilanes Me$_2$Si(3,5-R$_2$pz)$_2$ (R = H, Me)[88] and also the tridentate thioether ligands MeSi(CH$_2$SR)$_3$ (R = Me, Ph).[89] The three tricarbonyl complexes (Tps^{Me_2})M(CO)$_3$ (M = Cr, Mo, W) were readily prepared and fully characterized and make a very attractive triad of starting materials for reactivity studies, which are currently under way. Spectroscopic (IR, NMR) studies suggest that Tps^{Me_2} is electronically very similar to its tris(pyrazolyl)methane analogue HC(3,5-Me$_2$pz)$_3$ and also to the anionic tris(pyrazolyl)borate ligand Tp^{Me_2}. However, X-ray diffraction studies of the three octahedral and isostructural (Tps^{Me_2})M(CO)$_3$ complexes revealed that the cone angle of the silane ligand not only is moderately larger than that of Tp^{Me_2} but also approaches the value estimated for well-known "tetrahedral enforcer" ligands such as Tp$^{Bu^t}$. Last but not least, X-ray crystallographic data were also used to calculate a value of 1.59 Å for the covalent radius of tungsten(0) in an octahedral environment, a plausible estimate when compared to the reported covalent radii of Cr(0) and Mo(0).

Experimental Section

General Considerations. All reactions were performed under dry oxygen-free nitrogen in an Innovative Technology System One-M-DC glovebox or under argon using a combination of high-vacuum and Schlenk techniques.[90−92] Solvents were purified and degassed by standard procedures, and all commercially available reagents were used as received. M(CO)$_3$(NCMe)$_3$ (M = Cr, Mo)[93] and W(CO)$_3$(NCEt)$_3$[94] were prepared as reported. ^{1}H and ^{13}C NMR spectra were obtained on General Electric QE 300 or Varian Gemini (300 MHz) FT spectrometers. Chemical shifts (δ) are reported in parts per million relative to SiMe$_4$ (δ = 0 ppm) and were referenced internally with respect to the residual protio solvent resonances (δ 7.15 for C$_6$D$_5$*H*, δ 1.94 for CD$_2$*H*CN) or the solvent resonances (δ 128.0 for *C*$_6$D$_6$, δ 1.39 for *C*D$_3$CN); coupling constants are given in hertz (Hz). IR spectra were recorded as KBr pellets on a Midac Collegian FT spectrophotometer and are reported in cm^{-1}; relative intensities of the absorptions are indicated in parentheses (vs = very strong, s = strong, m = medium, w = weak). Electrospray ionization mass spectra were obtained on a PerSeptive Biosystems Mariner ESI-TOF mass spectrometer by direct infusion using acetonitrile solutions and a flow rate of 10 μL/min. Elemental analyses were determined by Atlantic Microlab, Inc. (Norcross, GA) or Desert Analytics (Tucson, AZ).

Synthesis of Li(3,5-Me$_2$pz). A stirred suspension of 3,5-dimethylpyrazole (4.00 g, 41.62 mmol) in pentane (70 mL) was treated with a solution of LiBu^n in hexanes (2.5 M, 18.0 mL, 45.0 mmol). While a clear colorless solution was obtained after about half of the LiBu^n was added, addition of the remaining LiBu^n led to the slow formation of a white precipitate suspended in a pale-yellow solution. After the reaction mixture was stirred for 1 h, the product was isolated by filtration, washed with pentane (2 × 15 mL), and dried in vacuo for 30 min (3.76 g, 88%). NMR data (in CD$_3$CN): ^{1}H δ 2.10 [s, 6 H, (C*H*$_3$)$_2$pz], 5.55 (s, 1 H, 4-*H* in 3,5-Me$_2$pz); ^{13}C δ 13.9 [q, $^{1}J_{C-H}$ = 125, 2 C, (*C*H$_3$)$_2$pz], 102.8 [d, $^{1}J_{C-H}$ = 164, 1 C, 4-*C* in 3,5-Me$_2$pz], 149.8 [s, 2 C, 3-*C* and 5-*C* in 3,5-Me$_2$pz]. IR data (cm^{-1}): 3199 (m), 3129 (m), 3108 (m), 3036 (w), 2930 (s), 2877 (m), 1595 (w), 1513 (vs), 1412 (s), 1317 (m), 1048 (m), 1019 (vs), 969 (m), 795 (s), 780 (s), 759 (s), 737 (s), 462 (m). Anal. Calcd for C$_5$H$_7$LiN$_2$: C, 58.8; H, 6.9; N, 27.5. Found: C, 59.0; H, 7.0; N, 27.4.

Synthesis of Tps^{Me_2}. MeSiCl$_3$ (1.35 mL, 11.5 mmol) was slowly added from a syringe to a stirred suspension of Li(3,5-Me$_2$pz) (3.50 g, 34.3 mmol) in pentane (150 mL), resulting in the initial formation of a clear solution and, within 15 min, the appearance of a fine white precipitate (LiCl). After being stirred for 2 h, the solution was filtered using a fritted funnel and the collected solid washed with pentane (2 × 20 mL). The solvent was removed under reduced pressure from the combined filtrate and washings to give a white solid, which was dried in vacuo for 30 min (3.59 g, 96%); mp = 120−123 °C. ^{1}H NMR data (in C$_6$D$_6$): δ 1.56 [s, 9 H, (C*H*$_3$)$_2$pz], 1.62 (s, 3 H, C*H*$_3$Si), 2.16 [s, 9 H, (C*H*$_3$)$_2$pz], 5.66 (s, 3 H, 4-*H* in 3,5-Me$_2$pz); ^{1}H NMR data (in CD$_3$CN): δ 1.19 (s, 3 H, C*H*$_3$Si), 1.63 [s, 9 H, (C*H*$_3$)$_2$pz], 2.18 [s, 9 H, (C*H*$_3$)$_2$pz], 5.97 (s, 3 H, 4-*H* in 3,5-Me$_2$pz); ^{13}C NMR data (in C$_6$D$_6$): δ 0.0 (q, $^{1}J_{C-H}$ = 124, 1 C, *C*H$_3$Si), 10.5 [q, $^{1}J_{C-H}$ = 128, 3 C, (*C*H$_3$)$_2$pz], 13.7 [q, $^{1}J_{C-H}$ = 127, 3 C, (*C*H$_3$)$_2$pz], 109.2 [d, $^{1}J_{C-H}$ = 171, 3 C, 4-*C* in 3,5-Me$_2$pz], 148.0 (s, 3 C, 3-*C* or 5-*C* in 3,5-Me$_2$pz), 153.9 (s, 3 C, 3-*C* or 5-*C* in 3,5-Me$_2$pz); ^{13}C NMR data (in CD$_3$CN): δ 0.0 (q, $^{1}J_{C-H}$ = 124, 1 C, *C*H$_3$Si), 10.9 [q, $^{1}J_{C-H}$ = 129, 3 C, (*C*H$_3$)$_2$pz], 13.8 [q, $^{1}J_{C-H}$ = 127, 3 C, (*C*H$_3$)$_2$pz], 110.2 [d, $^{1}J_{C-H}$ = 173, 3 C, 4-*C* in 3,5-Me$_2$pz], 149.5 (s, 3 C, 3-*C* or 5-*C* in 3,5-Me$_2$pz), 155.2 (s, 3 C, 3-*C* or 5-*C* in 3,5-Me$_2$pz). IR data (cm^{-1}): 3200 (w), 3111 (w), 3136 (w), 3086 (w), 3036 (w), 2961 (w), 2924 (w), 2874 (w), 1656 (w), 1595 (m), 1564 (s), 1466 (m), 1440 (m), 1420 (m), 1380 (w), 1371 (m), 1330 (m), 1316 (s), 1261 (m), 1155 (vs), 1090 (m), 1029 (m), 1020 (s), 969 (s), 833 (s), 812 (vs), 776 (s), 749 (m), 741 (s), 663 (w), 591 (m), 538 (vs), 475 (m), 430 (s), 402 (w). Anal. Calcd for C$_{16}$H$_{24}$N$_6$Si: C, 58.5; H, 7.4; N, 25.6. Found: C, 58.5; H, 7.4; N, 26.1.

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Table 3. Crystallographic Data for $(\mathrm{Tps^{Me_2}})\mathrm{M(CO)_3}$ Complexes

	M = Cr	M = Mo	M = W
formula	$C_{19}H_{24}CrN_6O_3Si$	$C_{19}H_{24}MoN_6O_3Si$	$C_{19}H_{24}N_6O_3SiW$
fw	464.53	508.47	596.38
cryst syst	monoclinic	orthorhombic	orthorhombic
space group	$P2_1/m$ (no. 11)	*Pnma* (no. 62)	*Pnma* (no. 62)
T, K	173(2)	173(2)	173(2)
a, Å	8.0132(6)	18.6624(4)	18.5761(2)
b, Å	13.7886(9)	14.1761(2)	14.1731(2)
c, Å	9.6481(7)	8.4402(2)	8.4049(2)
β, deg	97.1566(11)	90	90
V, Å^3	1057.72(13)	2232.94(8)	2212.83(4)
Z	2	4	4
D_c, g cm^{-3}	1.459	1.513	1.790
μ (Mo Kα), cm^{-1}	6.31	6.73	53.07
color, habit	yellow plate	yellow plate	yellow block
R_1/wR_2 [$I > 2\sigma(I)$] [a]	0.0638/0.1841	0.0359/0.1269	0.0289/0.1141
R_1/wR_2 (all data) [a]	0.0828/0.2041	0.0412/0.1337	0.0330/0.1221

[a] $R_1 = \sum(|F_o| - |F_c|)/\sum|F_o|$; $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)]^2\}^{1/2}$; $w^{-1} = \sigma^2(F_o) + (aP)^2 + bP$; $P = [2F_c^2 + \max(F_o^2,0)]/3$.

Synthesis of $(\mathrm{Tps^{Me_2}})\mathrm{Cr(CO)_3}$. (a) From $\mathrm{Cr(CO)_6}$. A stirred suspension of $\mathrm{Cr(CO)_6}$ (0.60 g, 2.74 mmol) and $\mathrm{Tps^{Me_2}}$ (0.90 g, 2.74 mmol) in methylcyclohexane (20 mL) was heated to reflux under argon for 7 h, resulting in the formation of a bright-yellow precipitate and a pale-yellow supernatant solution. After the reaction mixture was cooled to room temperature, the product was isolated by filtration, washed with pentane (20 mL), and dried in vacuo for 1 h (0.30 g, 24%). NMR data (in $\mathrm{CD_3CN}$): ^{1}H δ 1.56 (s, 3 H, CH_3Si), 2.40 [s, 9 H, (CH_3)$_2$pz], 2.74 [s, 9 H, (CH_3)$_2$pz], 6.08 (s, 3 H, 4-*H* in 3,5-Me$_2$pz); ^{13}C{^{1}H} δ 14.4 [s, 3 C, (*C*H$_3$)$_2$pz], 16.2 [s, 3 C, (*C*H$_3$)$_2$pz], 112.0 (s, 3 C, 4-*C* in 3,5-Me$_2$pz), 150.8 (s, 3 C, 3-*C* or 5-*C* in 3,5-Me$_2$pz), 160.0 (s, 3 C, 3-*C* or 5-*C* in 3,5-Me$_2$pz), 234.3 (s, 3 C, *C*O), *C*H$_3$Si was not located because of the low solubility of the complex. IR data (cm^{-1}): 2989 (w), 2932 (w), 1898 (vs), 1755 (vs), 1565 (m), 1480 (w), 1447 (m), 1412 (m), 1377 (m), 1336 (m), 1302 (m), 1285 (m), 1163 (m), 1086 (w), 1032 (m), 976 (m), 790 (m), 700 (w), 670 (m), 553 (w), 522 (m). ESI-MS data (*m*/*z* (relative intensity)): 935 (43), 464 (22), 380 (47), 317 (100), 263 (97). Anal. Calcd for $C_{19}H_{24}CrN_6O_3Si$: C, 49.1; H, 5.2; N, 18.1. Found: C, 48.8; H, 5.4; N, 17.7.

(b) From $\mathrm{Cr(CO)_3(NCMe)_3}$. A colorless solution of $\mathrm{Tps^{Me_2}}$ (0.75 g, 2.28 mmol) in acetonitrile (20 mL) was added to a stirred orange-yellow solution of $\mathrm{Cr(CO)_3(NCMe)_3}$ (0.59 g, 2.28 mmol) in the same solvent (10 mL), resulting in the formation, within 10 min, of a bright-yellow precipitate. After being stirred for 2.5 h, the suspension was concentrated under reduced pressure to ca. 5 mL and diethyl ether (25 mL) was added. The product was isolated by filtration from the greenish supernatant solution, washed with diethyl ether (25 mL), and dried in vacuo for 1.5 h (0.73 g, 69%). The product exhibits the same spectroscopic properties as those of the compound obtained in (a).

Synthesis of $(\mathrm{Tps^{Me_2}})\mathrm{Mo(CO)_3}$. (a) From $\mathrm{Mo(CO)_6}$. A stirred suspension of $\mathrm{Mo(CO)_6}$ (0.24 g, 0.91 mmol) and $\mathrm{Tps^{Me_2}}$ (0.30 g, 0.91 mmol) in methylcyclohexane (15 mL) was heated to reflux under argon for 16 h, resulting in the formation of a yellow precipitate and a brown supernatant solution. After the reaction mixture was cooled to room temperature, the product was isolated by filtration, washed with pentane (20 mL), and dried in vacuo for 1 h (0.33 g, 71%). NMR data (in $\mathrm{CD_3CN}$): ^{1}H δ 1.61 (s, 3 H, CH_3Si), 2.43 [s, 9 H, (CH_3)$_2$pz], 2.63 [s, 9 H, (CH_3)$_2$pz], 6.11 (s, 3 H, 4-*H* in 3,5-Me$_2$pz);^{13}C{^{1}H} δ 14.7 [s, 3 C, (*C*H$_3$)$_2$pz], 16.4 [s, 3 C, (*C*H$_3$)$_2$pz], 111.8 (s, 3 C, 4-*C* in 3,5-Me$_2$pz), 151.3 (s, 3 C, 3-*C* or 5-*C* in 3,5-Me$_2$pz), 159.7 (s, 3 C, 3-*C* or 5-*C* in 3,5-Me$_2$pz), 228.8 (s, 3 C, *C*O), *C*H$_3$Si was not located because of the low solubility of the complex. IR data (cm^{-1}): 3011 (w), 2936 (w), 1896 (vs), 1755 (vs), 1561 (m), 1454 (m), 1400 (m), 1374 (m), 1369 (m), 1327 (m), 1084 (w), 1036 (m), 977 (m), 803 (m), 666 (m), 593 (w), 523 (m). ESI-MS data (*m*/*z* (relative intensity)): 1023 (12), 510 (27), 423 (23), 283 (86), 265 (90), 211 (100). Anal. Calcd for $C_{19}H_{24}MoN_6O_3Si$: C, 44.9; H, 4.8; N, 16.5. Found: C, 43.6; H, 4.6; N, 16.2.

(b) From $\mathrm{Mo(CO)_3(NCMe)_3}$. A colorless solution of $\mathrm{Tps^{Me_2}}$ (0.76 g, 2.31 mmol) in acetonitrile (25 mL) was added to a stirred yellow solution of $\mathrm{Mo(CO)_3(NCMe)_3}$ (0.70 g, 2.31 mmol) in the same solvent (15 mL), resulting in the formation, within 15 min, of a yellow precipitate. After being stirred for 3 h, the suspension was concentrated under reduced pressure to ca. 10 mL and diethyl ether (25 mL) was added to the reaction mixture. The product was isolated by filtration from the brownish supernatant, washed with diethyl ether (20 mL), and dried in vacuo for 1 h (0.83 g, 71%). The product exhibits the same spectroscopic properties as those of the compound obtained in (a).

Synthesis of $(\mathrm{Tps^{Me_2}})\mathrm{W(CO)_3}$. A colorless solution of $\mathrm{Tps^{Me_2}}$ (0.76 g, 2.31 mmol) in tetrahydrofuran (10 mL) was added dropwise to a stirred yellow solution of $\mathrm{W(CO)_3(NCEt)_3}$ (1.00 g, 2.31 mmol) in the same solvent (100 mL), resulting in the formation, within 1 min, of a yellow precipitate and an orange-brown supernatant solution. After being stirred for 30 min, the suspension was concentrated under reduced pressure to ca. 50 mL. The yellow product was isolated by filtration, washed with diethyl ether (20 mL) and then with pentane (20 mL), and dried in vacuo for 1 h (1.05 g, 76%). NMR data (in $\mathrm{CD_3CN}$): ^{1}H δ 1.63 (s, 3 H, CH_3Si), 2.43 [s, 9 H, (CH_3)$_2$pz], 2.66 [s, 9 H, (CH_3)$_2$pz], 6.14 (s, 3 H, 4-*H* in 3,5-Me$_2$pz); ^{13}C{^{1}H} δ 14.8 [s, 3 C, (*C*H$_3$)$_2$pz], 17.3 [s, 3 C, (*C*H$_3$)$_2$pz], 111.9 (s, 3 C, 4-*C* in 3,5-Me$_2$pz), 151.4 (s, 3 C, 3-*C* or 5-*C* in 3,5-Me$_2$pz), 160.3 (s, 3 C, 3-*C* or 5-*C* in 3,5-Me$_2$pz), 223.4 (s, 3 C, *C*O), *C*H$_3$Si was not located because of the low solubility of the complex. IR data (cm^{-1}): 3005 (w), 2929 (w), 1887 (vs), 1747 (vs), 1566 (m), 1560 (m), 1412 (m), 1400 (m), 1375 (m), 1369 (m), 1333 (m), 1296 (m), 1288 (m), 1162 (m), 1150 (m), 1084 (w), 1037 (m), 978 (w), 804 (s), 665 (w). ESI-MS data (*m*/*z* (relative intensity)): 1193 (4), 595 (100), 512 (60), 341 (59), 265 (51), 211 (57). Anal. Calcd for $C_{19}H_{24}N_6O_3SiW$: C, 38.3; H, 4.1; N, 14.1. Found: C, 38.7; H, 4.2; N, 13.2.

X-ray Structure Determinations. Crystal data collection and refinement parameters are given in Table 3. Suitable crystals for data collection were selected and mounted in nitrogen-flushed, thin-walled capillaries. Data were collected on a Siemens P4/CCD system using Mo Kα radiation ($\lambda = 0.710\,73$ Å). The systematic absences in the diffraction data were consistent with the space groups $P2_1$ and $P2_1$/m for $(\mathrm{Tps^{Me_2}})\mathrm{Cr(CO)_3}$ and $Pna2_1$ and *Pnma* for $(\mathrm{Tps^{Me_2}})\mathrm{M(CO)_3}$ (M = Mo, W). *E*-statistics suggested the centrosymmetric space group options, which yielded chemically reasonable and computationally stable results for the refinement. The structures of $(\mathrm{Tps^{Me_2}})\mathrm{M(CO)_3}$ (M = Mo, W) are isomorphous. All structures were solved using the Patterson function or initiated from analogue coordinates, completed by subsequent difference Fourier syntheses and refined by full-matrix least-squares procedures. All non-hydrogen atoms were refined with anisotropic displacement coefficients, and the hydrogen atoms were treated as idealized contributions. All software and sources of the scattering factors are contained in the SHELXTL NT 5.10 program library (G. Sheldrick, Siemens XRD, Madison, WI).

Acknowledgment. We thank the Camille and Henry Dreyfus Foundation Faculty Start-Up Grant Program for Undergraduate Institutions, Research Corporation for a Cottrell College Science Award, the Donors of the Petroleum Research Fund, administered by the American Chemical Society, and The University of North Carolina at Charlotte for support of this research. We also acknowledge generous funding from the National Science Foundation (Grant CHE-9871160) for the purchase of the mass spectrometry instrumentation and Professor Brian T. Cooper (UNC Charlotte) for his assistance with the ESI-MS experiments.

Supporting Information Available: ORTEP diagrams of the Mo and W analogues of $(\mathrm{Tps}^{\mathrm{Me}_2})\mathrm{Cr(CO)}_3$ and an X-ray crystallographic file in CIF format for the structure determinations of $(\mathrm{Tps}^{\mathrm{Me}_2})\mathrm{M(CO)}_3$ (M = Cr, Mo, W). This material is available free of charge via the Internet at http://pubs.acs.org.

IC990945L