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A metal (^{51}V, ^{55}Mn, ^{59}Co) NMR investigation of the electron-deficient complexes $V(CO)_3$tmpo, $Mn(CO)_3$tmpo and $Co(CO)_2$tmpo (tmpo = 2,2,6,6-tetramethylpiperidyl-1-oxyl)

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Abstract

The diamagnetic, electron-deficient complexes $V(CO)_3$tmpo, $Mn(CO)_3$tmpo and $Co(CO)_2$tmpo, containing the tmpo ligand in the η^2-bond mode, have been investigated by metal NMR spectroscopy. The V and Mn compounds exhibit extremely low metal shieldings, which can be rationalized in terms of the low polarizability of the NO functionality of the 4-electron donating tmpo(1 –) or of low-lying electronic excitations between predominantly *d*-type molecular orbitals associated with strained three-membered metallacycles.

Introduction

2,2,6,6-Tetramethylpiperidyl-1-oxyl (tmpo) is a radical scavenger which has been employed, inter alia, to trap radicals such as $Mn(CO)_5^{\bullet}$ and $Co(CO)_4^{\bullet}$ produced in the photolytic fission of the metal–metal bonds of the dimers $Mn_2(CO)_{10}$ and $Co_2(CO)_8$. The reaction products are $Co(CO)_2$tmpo (**1**) [1] and $Mn(CO)_3$tmpo (**2**) [2]. Reaction of tmpo with the 17-electron complex $V(CO)_6$ yields $V(CO)_3$tmpo (**3**) [3]. The molecular structures of **1** and **2** (Fig. 1) have been determined by single crystal X-ray diffraction spectrometry; the ligand tmpo is bonded in the η^2-mode. The cobalt complex **1** is planar. The manganese complex **2** consists of a trigonal pyramidal $\{Mn(CO)_3\}$ moiety with the NO linkage of tmpo centred at the remaining fourth position of an overall tetrahedral arrangement, and aligned with one of the Mn–C–O bonds. We propose a similar structure for the vanadium compound **3**.

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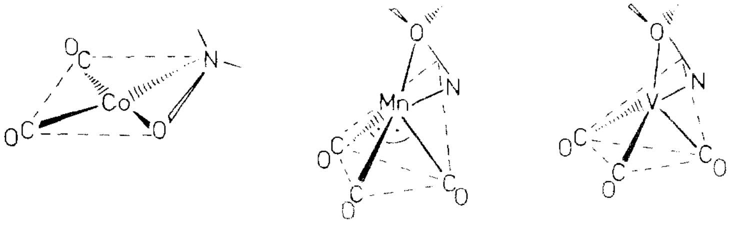
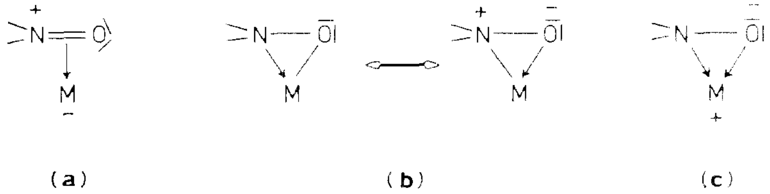


(1) (2) (3)

Fig. 1. Structures of the complexes $Co(CO)_2$tmpo (**1**) and $Mn(CO)_3$tmpo (**2**) according to refs. [1] and [2], and proposed structure of $V(CO)_3$tmpo (**3**).



Scheme 1

Tmpo is an interesting ligand in that it can, depending on the electron distribution introduced into the complex, provide a varying number of electrons (Scheme 1). The most common description involves the interaction between a positive metal centre, M(1 +), and negatively charged tmpo(1 −) (**c** in Scheme 1) which, comparable to the η^2-bonded hydroxylamido ligand, acts as a four-electron donating system. In this description, the complexes are electronically unsaturated 16- (**1** and **2**) and 14-electron complexes (**3**), respectively. The N–O bond lengths in **1** and **2** are slightly greater than in tmpo itself, exceeding the N–O bond length in uncoordinated tmpo by 13 and 10 pm [1,2], which is not convincing support for a formulation as tmpo(1 −) and could just as well be a consequence of metal-to-ligand π back-donation into appropriate antibonding orbitals of the tmpo ligand associated with the NO function. Support for the M(1 +)/tmpo(1 −) interaction comes, however, from the CO stretching modes (Table 1), which are nicely consistent with a carbonyl–metal unit containing the metal in the +I oxidation state.

Table 1

IR data (CO stretching region) in n-pentane

Complex	$\nu(CO)$ (cm^{-1})
$Co(CO)_2$tmpo(**1**)	2033s, 1949s
$Mn(CO)_3$tmpo(**2**)	2031s, 1933s, 1915s
$V(CO)_3$tmpo(**3**)	2027s, 1935vs, 1892vs

NMR investigation

In order to gain further insight into the electron distribution within the three-membered metallocycles, we have looked at the metal NMR spectra of **1**, **2** and **3**. Nuclear data for the nuclei ^{51}V, ^{55}Mn and ^{59}Co are collected in Table 2. All three metal nuclei have a spin $> 1/2$ and hence an electric nuclear quadrupole moment, i.e. relaxation rates are governed by the quadrupole mechanism and broad resonance lines arise except where the point-charge model predicts a zero field gradient [4]. In the case of **1** and **2**, the widths of the resonance signals at half-height, $W_{1/2}$, are 6.8 (**1**) and 9.4 kHz (**2**), i.e. there is a non-zero field gradient at the metal nuclei. A rather sharp line (< 0.2 kHz) is observed for the vanadium complex **3**. Although this is partly due to the low quadrupole moment of the ^{51}V nucleus, the narrow line also indicates that in this case (and in contrast to the manganese complex **2**) the tetrahedral array is constructed in a manner which gives rise to a minimum electric field gradient at the vanadium nucleus [4]. Comparison of the intensity patterns of the $\nu(CO)$ of **2** and **3** (Table 1) in fact shows that the arrangement of the ligands in the two complexes is different (in **2**, the CO groups are orthogonal).

The most striking feature arising from the the NMR results is the considerable deshielding of the metal nuclei in the tmpo complexes compared with those in, e.g., the carbonylmetalates or, in the case of **2** and **3**, complexes containing three-electron donor ligands (Table 3). Further, there is an obvious down-field shift of $\delta(M)$ with respect to carbonyl complexes with the metal centre in the +I state.

The $\delta(^{51}V)$ value for **3** is the lowest shielding yet observed for a carbonylvanadium compound, and $\delta(^{55}Mn)$ for **2** is, next to the value for *fac*-$[Mn(CO)_3(NCMe)_3]^+$ (+490 ppm) [6], at extreme low-field of the range for manganese complexes *. It is tempting to attribute the low shielding for these nuclei to the lack of electrons. But neither is the expected trend observed (the 14-electron complex **3** should exhibit the greatest effect) nor is this view consistent with the chemical shift values for the electronically saturated complexes $Co(CO)_3NO$ on the one hand, and the electron-deficient $Co(CO)_2$tmpo on the other (Table 3).

A more comprehensive explanation has to take into account the molecular parameters influencing the values of the shielding of non-proton nuclei via the

Table 2

Nuclear data

Nucleus	Abundance (%)	Spin	Quadrupole moment [a] ($\times 10^{-28}$ m^2)	Relative receptivity [b] ($^1H = 1$)
^{51}V	99.76	7/2	−0.0515	5.52
^{55}Mn	100	5/2	0.33	2.88
^{59}Co	100	7/2	0.42	4.96

[a] According to the Bruker Almanac 1987. [b] For an equal number of nuclei per unit volume; at constant measuring frequency.

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* A collection of data and the discussion of many general aspects of metal NMR parameters are contained in the following surveys: ^{51}V [5]; ^{51}V, ^{55}Mn and ^{59}Co [6–8].

Table 3

Metal NMR data for **1**, **2** and **3** and selected carbonyl complexes of V, Mn and Co [a,b]

Complex	$\delta(^{51}V)$	$\delta(^{55}Mn)$	$\delta(^{59}Co)$	Refs.
$V(CO)_3$tmpo(**3**)	−430			[c]
$[V(CO)_6]^-$	−1952			[5,6]
$V(CO)_5NO$	−1489 [d]			[9]
$V(CO)_3(dppe)$-η^3-C_3H_5 [e]	−1492			[5]
$V(CO)_3(dppe)$-η^2-acyl [e,f]	−931			[10]
$V(CO)_3$-η^7-C_7H_7	−1485			[11]
$[V(CO)_3$-η^6-Tol$]^-$	−1660			[11]
$Mn(CO)_3$tmpo(**2**)		+380		[c]
$[Mn(CO)_5]^-$		−2780		[6,12]
$Mn(CO)_4NO$		−1730		[c]
$Mn(CO)_4Cl(PEtPh_2)$		−1080		[13]
$Co(CO)_2$tmpo(**3**)			−1205	[c]
$[Co(CO)_4]^-$			−3100	[6,12]
$Co(CO)_3NO$			−1365	[13]
$Co(CO)_4SnCl_3$			−2950	[6,12]

[a] In ppm at room temperature. $\delta(^{51}V)$ relative to $VOCl_3/CD_3Cl$. $\delta(^{55}Mn)$ relative to aqueous $K[MnO_4]$, $\delta(^{59}Co)$ relative to aqueous $K_3[Co(CN)_6]$. Half-widths for the tmpo complexes: **3**, 0.2; **2**, 9.4; **1**, 6.8 kHz. [b] For additional chemical shift data see, e.g. the listings in refs. [5,6,8,12]. [c] This work. [d] At 245 K. [e] dppe = $Ph_2PCH_2CH_2PPh_2$. [f] η^2-acyl = cyclo-C_3H_5CO. For other acyl complexes see ref. [10].

paramagnetic deshielding contribution σ(para) to the overall shielding σ (eq. 1):

$$\sigma = \sigma(\text{dia}) - \sigma(\text{para}) = \sigma(\text{dia}) - b \cdot \overline{\Delta E^{-1}}\langle r^{-1}\rangle_{3d}\overline{C^2_{3d}} \qquad (1)$$

σ(dia) is constant to within several ppm and b is a constant. The three parameters to be considered here are the mean HOMO–LUMO gap $\overline{\Delta E}$, the distance of the metal valence-d electrons from the metal nucleus, r_{3d} ($\langle r^{-3}\rangle$ is the quantum-mechanical expectation value for r^{-3}), and the metal-3d LCAO coefficients C_{3d} of the HOMO and LUMO(s) taking part in electronic transitions. The quantities are interrelated, and it is usually impossible (and unreasonable) to separate out one of them in order to derive simple correlations with σ. Several general trends can, however, be deduced from data in the literature: For low-valent complexes, low metal shielding σ goes along with (i) weak π accepting ligands, (ii) weakly polarizable ligands, (iii) ligands with highly electronegative coordinating functions, and (iv) bulky ligands and ligands giving rise to strained ring structures.

Tmpo does not seem to be a weak ligand, since it forms stable diamagnetic complexes with the carbonylmetal fragment, there being no low-frequency shift of the CO-stretching bands. Polarizability (ii) and electronegativity (iii) effects are closely connected with each other and with further quantities such as the ligand nephelauxetic effect, the Pearson basicity etc. Their influence upon σ(para) is mainly via $\langle r^{-3}\rangle C^2$. Hard ligands (i.e. those with high electronegativity values and low polarizability) will increase σ(para) through an increase of C_{3d} and a decrease of r_{3d}. Tmpo, in its formulation as a hydroxylamido function, belongs to this ligand category. The polarizability perpendicular to the N–O bond is particularly low, and gives rise to an pronounced low-field shift of the metal resonance. The deshielding contribution of the η^2- as compared to the η^1-coordination has been noted, inter alia, for carbonylvanadium complexes containing the η^2-acyl [10] and η^2-alkene groups [14].

Alternatively, the deshielding can be interpreted as a steric effect ((iv) in the above listing), originating from strains in the three-membered $\overline{M-N-O}$ cycle. Ring-strains in chelate structures cause overlap perturbations (angle distortions) between metal and ligand orbitals, resulting in small ΔE and large C_{3d} values. The two factors, according to eq. 1, point in the same direction: an increase of σ(para) and a decrease of σ.

In the vanadium system, there is substantial evidence for this deshielding effect in low-valent complexes * containing three-membered ring structures. Examples are the previously mentioned carbonylvanadium complexes with side-on coordinated acyl ligands (cf. also Table 3) and alkenes. For the latter, the deshielding with respect to η^1-coordinated carbon ligands (CNR, CO) amounts to ca. 250 ppm [14]. There are no metal NMR data available for chelate-three ring structures in low-valent Mn and Co complexes. Data exist, however, for (strained) four-ring structures: in all four-membered rings, the metal nuclei are deshielded with respect to corresponding, unstrained, five-rings.

Examples are $\{M\overparen{n(C}O)_4\}_2\text{-}\underline{\mu}\text{-}\{P(CF_3)_2\}\mu\text{-}Y$ ($Y = P(CF_3)_2$ and $S{=}P(CF_3)_2$; $\Delta\delta =$ 360 ppm [15]), $[Co(\widehat{LL})_3]^{3-}$ ($\widehat{LL} = CO_3^{2+}$, $C_2O_4^{2-}$; $\Delta\delta = 900$ ppm [6]) and, in the vanadium system, $Cp\overline{V(CO)_2Ph_2P(CH_2)_nP}Ph_2$ ($n = 1, 2$; $\Delta\delta = 240$ ppm [6]); these trends support the view that there is a deshielding effect with ring strains in low-valent (open-shell) transition metal complexes (the normal chelate effect).

Conclusion

The ligand tmpo coordinates side-on to metal centres such as low-valent V, Mn and Co, forming the diamagnetic complexes $V(CO)_3$tmpo (**3**), $Mn(CO)_3$tmpo (**2**) and $Co(CO)_2$tmpo (**1**), which are electron-deficient, if tmpo is considered a two- to four-electron donor (Scheme 1). The tmpo induces a large deshielding σ at the metal nuclei ^{51}V, ^{55}Mn and ^{59}Co relative to the carbonylmetalates (cf. Table 3). The extent of deshielding induced by tmpo, relative with the overall shielding ranges of the three nuclei (^{51}V and ^{55}Mn ca. 3,500, ^{59}Co ca. 20,000 ppm [6,7]) is least pronounced in the cobalt complex.

The deshielding effect induced by tmpo can be explained in terms of the high electronegativity/low polarizability of the η^2-bonded NO functionality, or of a steric component imparted by overlap disturbations in the three-membered metallacycle. The two views, which emphasize influences upon the paramagnetic deshielding contribution to the overall shielding (eq. 1) via electron delocalization (r_{3d}^{-3}) and electronic excitations (ΔE^{-1}), respectively, are interchangeable. In either view, large metal $3d$ contributions (C_{3d}) to the relevant orbitals are an important factor contributing to the deshielding. Tmpo is from the NMR point of view a hard ligand but it is nevertheless an effective π electron-withdrawing ligand.

Experimental

The complexes $Co(CO)_2$tmpo (**1**), $Mn(CO)_3$tmpo (**2**) and $V(CO)_3$tmpo (**3**) were prepared by photo-reaction between tmpo and $Co_2(CO)_8$ or $Mn_2(CO)_{10}$, or by

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* For η^2-hydroxylamido complexes of V(5+) [16], the chelate effect is inverse owing to d-electron depletion of molecular orbitals in the strained system.

Table 4

Details of the NMR measurements

Compound	Standard [B_s [a] (T)]	Sweep (mT)	Modulation (mT)	*Rf*-field (dB) [b]	No. of scans [tc [c] (s)]
$Co(CO)_2$tmpo(**1**)	$K_3[Co(CN)_6]/H_2O$ [1.58446]	5	0.16	20	43 [0.5]
$Mn(CO)_3$tmpo(**2**)	$K[MnO_4]/H_2O$ [1.51680]	10	0.25	10	41 [0.5]
$V(CO)_3$tmpo(**3**)	$VOCl_3/CDCl_3$ [1.42970]	0.5	0.013	5	4 [0.2]

[a] B_s = magnetic field for the standard. Central magnetic field $B_0 = 1.5865$ (**1**), 1.5150 (**2**), 1.4303 (**3**) T. [b] Maximum setting: 0 dB. [c] Time constant; scan time = 2 min.

direct reaction between tmpo and $V(CO)_6$ in inert solvents (alkanes), and characterized by, inter alia, X-ray crystallography (**1** and **2** only), IR and mass spectrometry [1–3].

^{51}V, ^{55}Mn and ^{59}Co NMR spectra were obtained on a Bruker SWL 3-100 wide-line instrument at 16.00016 MHz as ca. 0.05 *M* n-heptane (**1**, **2**) or n-hexane solutions (**3**) contained in 14 mm diameter tubes. The solutions were prepared under Ar. Measurement details are summarized in Table 4. Estimated errors for the shift values are ±25 ppm (**1** and **2**) and ±10 ppm (**3**), for $W_{1/2}$ ±5%.

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