First example of a metal(0) carbonyl complex with a paramagnetic nitronyl nitroxide-substituted triphenylphosphine ligand

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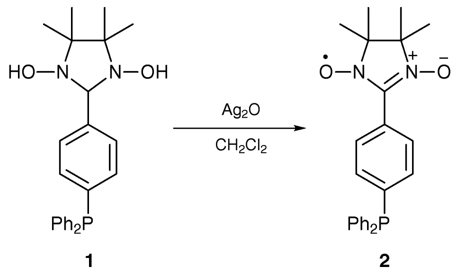
A stable metal(0) carbonyl complex with a paramagnetic nitronyl nitroxide-substituted triphenylphosphine ligand has been prepared and gives rise in the crystal to a 1D-array of ferromagnetically coupled $S = 1/2$ spins.

In the course of our research on the tailoring of organic molecules likely to be building blocks for organic[1] and metallo-organic[2] magnetic materials we recently synthesized a series of novel open-shell phosphine derivatives.[3] These compounds comprise a triphenylphosphine core and a nitronyl nitroxide moiety. Phosphines have been chosen in view of their ability to be very good ligands for a large variety of metals in low oxidation states. Moreover, depending on the metal involved in the complex formation process, a selectivity in the coordination site of the phosphine derivative, *i.e.* P *vs.* nitroxyl O atoms, is anticipated due to the characteristics of the heteroatoms likely to interact with the metal centre. We now report that (4-nitronyl nitroxide-phenyl)diphenylphosphine **2**, can be reacted with a metal carbonyl compound, [Mo(CO)$_5$(thf)], to afford a stable Mo(0) complex, **4**, displaying a phosphine ligand with an unpaired electron. The syntheses and magnetic properties of both **2** and **4** as well as the X-ray structure of **4** are presented.

The synthesis of phosphine **2** has already been briefly reported.[3] However, considerable variations in the efficiency of the final oxidation step to produce the radical were observed. We found that the use of Ag$_2$O instead of PbO$_2$ as oxidant gave reproducibly **2** from **1** in yields up to 70% [eqn. (1)]. The complex [Mo(CO)$_5$(**2**)], **4**, was synthesized according to two different routes (routes A and B, Scheme 1). Following route A, the reaction of phosphine **2** with the adduct [Mo(CO)$_5$(thf)] in thf gave **4** as a stable deep-blue compound which could be purified by column chromatography. The alternative synthesis (route B) consists of the reaction of 1,3-dihydroxy-2-[4′-(diphenylphosphine)phenyl]-4,4,5,5-tetramethyl-imidazoline **1** and [Mo(CO)$_5$(thf)] to give the radical precursor complex [Mo(CO)$_5$(**1**)] **3**. The latter was subsequently oxidized by NaIO$_4$ to afford **4**. Route B is very convenient since during the oxidation step to generate the radical, the phosphorus atom is effectively protected from oxidation by its bonding to the Mo centre.



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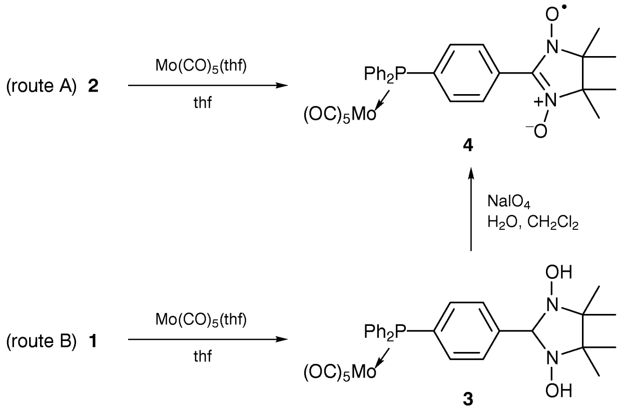

Scheme 1

An X-ray crystal structure† established that **4** is indeed a Mo(CO)$_5$ moiety substituted by phosphine **2**. An ORTEP view is presented in Fig. 1 with selected bond lengths and angles. Interestingly it appears that in the solid state the nitronyl nitroxide moiety tends to be coplanar with the substituted phenyl. This should ensure spin polarization over the whole molecule and especially on the adjacent phenyl group.[4] A view of the crystal packing shows that the nitronyl nitroxide groups are aligned in a head to tail fashion along the *b* axis to form pseudo chains (Fig. 2). It is noticeable that within these alignments the shortest intermolecular distances involving the nitroxyl O atoms are found with H in the *ortho* position of the neighbouring nitronyl nitroxide substituted phenyl group [O(6)···H(10) 2.66 Å and O(7)···H(8) 2.81 Å] and the H atom in the *meta* position [O(6)···H(11) 2.86 Å and O(7)···H(7) 2.821 Å]. The separation between two neighbouring nitroxide O-atoms O(6) (x, y, z) and O(7) $(-x + \frac{1}{2}, y - \frac{1}{2}, -z)$ is 3.892 Å. The shortest interchain distances involving O(6) and O(7) are to H(21) (2.752 Å) and to H(27) (3.085 Å), respectively, in the *meta* position of non-substituted phenyl groups. However, the interchain separation of the spin carriers is large, and the

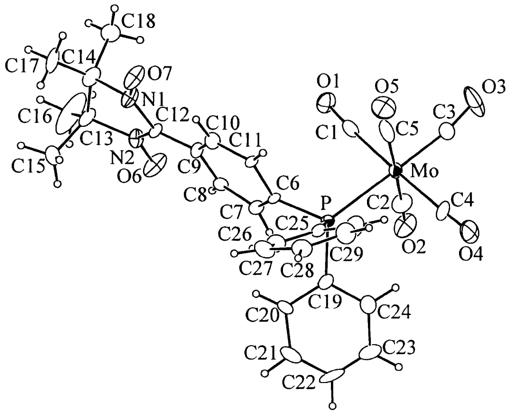

Fig. 1 View of molecule **4** showing the atom labelling scheme. Selected bond lengths (Å): N(1)–O(7) 1.266(16), N(2)–O(6) 1.304(17), N(1)–C(12) 1.37(2), N(2)–C(12) 1.32(2), C(12)–C(9) 1.479(9), C(6)–P 1.835(6), P–Mo 2.546(2), C(3)–Mo 2.005(8), Mo–(other CO) 2.031 (mean). Angle between mean planes N(1)–C(12)–N(2) and C(9)–C(10)–C(8) 3.9°.

magnetic interaction is assumed to occur mainly within the molecules aligned along the *b* axis.

The temperature (*T*) dependence of the molar magnetic susceptibility (χ_M) of compounds **2** and **4** was measured in the temperature range 2–300 K using a SQUID susceptometer, Fig. 3 shows the $\chi_M T$ *vs.* *T* plots. At high temperature (50–300 K), for both **2** and **4**, $\chi_M T$ is *ca.* 0.37 cm^3 K mol^{-1}, the expected value for non-correlated $S = 1/2$ spins. As the temperature is lowered from *ca.* 50 K down to 2 K the compounds do not behave in the same way. For phosphine **2**, $\chi_M T$ decreases very rapidly as *T* is lowered whereas for complex **4**, $\chi_M T$ increases more and more rapidly to reach 0.44 cm^3 K mol^{-1} at 2 K, the lowest temperature investigated. These behaviours are characteristic for intermolecular antiferromagnetic and ferromagnetic interactions in **2** and **4**, respectively. The intermolecular O(6)···C(10) and O(7)···C(8) proximities are anticipated to play an important role in the ferromagnetic interactions observed for complex **4** at low temperature. Taking into account a McConnell-type spin polarization mechanism,[5] the through space magnetic interaction between the nitroxide moiety and the *ortho* position of the neighbouring phenyl group should indeed lead the spins to align ferromagnetically.[6] The magnetic data of compound **4** have been analysed in terms of a one-dimensional Heisenberg chain model for ferromagnetically coupled $S = 1/2$ spins.[7] This model leads to an intrachain interaction parameter equal to $J = 0.26$ cm^{-1} (with $H = -JS_i \cdot S_{i+1}$).

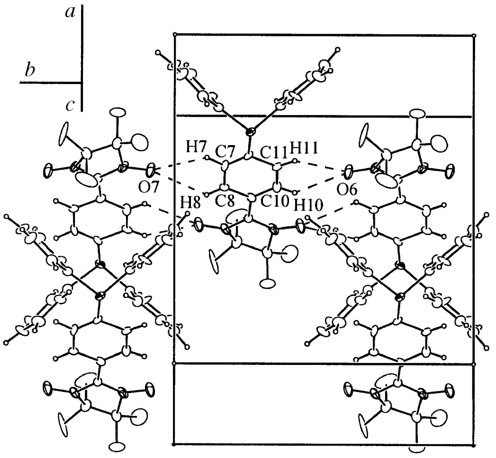

Fig. 2 View of the crystal lattice along the *b* direction showing the spin carriers alignment [the Mo(CO)$_5$ moieties along the *c* axis have been omitted]. Selected intermolecular distances (Å): O(6)···O(7) 3.892(8), O(6)···C(10) 3.33(2), O(6)···H(10) 2.66, O(6)···C(11) 3.40(2), O(6)···H(11) 2.86, O(7)···C(7) 3.472(19), O(7)···H(7) 2.821, O(7)···C(8) 3.44(2), O(7)···H(8) 2.81. Mean angle between two adjacent nitronyl nitroxide groups 0°.

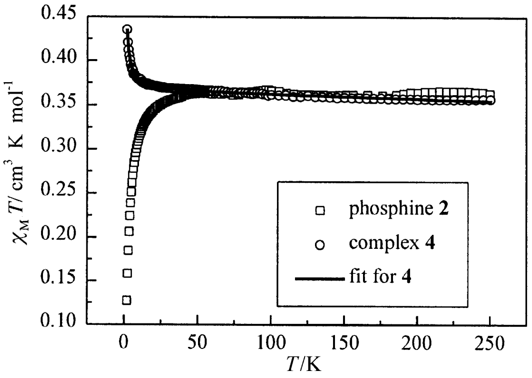

Fig. 3 Temperature dependence of $\chi_M T$ for the phosphine **2** and the complex **4**. The solid line represents the analytical fit based on a chain model of $S = 1/2$ spins in ferromagnetic interaction.

Compound **4**, obtained in one step from phosphine **2**, illustrates the possibility of switching the solid state magnetic behaviour, from antiferromagnetic in **2** to ferromagnetic in **4**, by small chemical alterations of a molecular brick. An interesting aspect of complex **4** consists of its overall tetrahedral geometry. However, the spin carrier is only on one phenyl group, *i.e.* in one direction. In order to increase the magnetic dimensionality of the network, polyradical species have to be considered.

Experimental

Reagent grade chemicals were used as received. THF was distilled from sodium benzophenone ketyl under nitrogen, prior to use. Silica gel (70–230 mesh) was used for chromatographic separations.

Synthesis of 2

Ag_2O (0.714 mmol, 165 mg) was added to a suspension of **1**[3] (0.476 mmol, 200 mg) in CH_2Cl_2 (30 mL). After about 30 min the solution turned blue. The reaction was monitored by TLC (silica, CH_2Cl_2) and stopped before the formation of a phosphine oxide derivative, indicated by the presence of a blue spot staying at the reference line. The reaction mixture was filtered through Celite® and the solvent removed *in vacuo* to give **2** as a blue oil which crystallised by addition of Et_2O. Anal. Calc. (found) for $C_{25}H_{26}N_2P$: C 71.93 (72.04), H 6.28 (6.36), N 6.71 (6.60%). IR (KBr, cm^{-1}): 1434 m, 1419 s, 1388 m, 1363 vs, 751 m, 697 vs, 508 m. UV–Vis (CH_2Cl_2): λ/nm (ε, dm^3 mol^{-1} cm^{-1}), 632(360), 595(360), 375(10 300), 300(14 400), 272(14 600).

Synthesis of 4 (route B)

A solution of $[Mo(CO)_5(thf)]$[8] in thf, prepared from $Mo(CO)_6$ (0.583 mmol, 154 mg), was added to a solution of **1** (0.697 mmol, 293 mg) in thf. After 30 min stirring, the solvent was removed *in vacuo* to give **3** as a white powder which was dissolved in CH_2Cl_2, and $NaIO_4$ (0.777 mmol, 166 mg) in H_2O added, leading to a blue solution. Compound **4** was extracted with CH_2Cl_2 and chromatographed (Silica gel/CH_2Cl_2) to give **4**, as a blue crystalline solid, after removal of the solvent [90 mg; 27% based on $Mo(CO)_6$]. Anal. Calc. (found) for $C_{30}H_{26}N_2PMo$: C 55.14 (54.35), H 4.01 (4.37), N 4.29 (4.07%). IR (CH_2Cl_2, cm^{-1}): 2073 m, 1990 w, 1946 vs. UV–Vis (CH_2Cl_2): λ/nm (ε/dm^3 mol^{-1} cm^{-1}), 597(350), 377(12 100), 360(8200).

Notes and references

† *Crystal data for* **4**: $C_{30}H_{26}N_2O_7PMo$, ($M = 653.4$, monoclinic, space group $C2$, $a = 14.860(10)$, $b = 13.641(2)$, $c = 15.399(7)$ Å, $\beta = 103.81(2)°$, $V = 3031(3)$ Å^3, $Z = 4$, $\mu = 0.533$ mm^{-1}. 3937 Reflections were measured (3794 unique), final $R1$ [$I > 2\sigma(I)$] = 0.0455, $wR2 = 0.0938$. The intensities were collected with an Enraf-Nonius CAD4 diffractometer using monochromated Mo-Kα radiation. The structure was solved by direct methods (SHELXS-86)[9] and refined by full-matrix least squares methods (SHELXL-97).[10] CCDC reference number 440/071. See http://www.rsc.org/suppdata/njc/1998/1333/ for crystallographic files in .cif format.

1 J. P. Sutter, A. Lang, O. Kahn, C. Paulsen, L.Ouahab and Y. Pei, *J. Magn. Magn. Mater.*, 1997, **171**, 147; A. Lang, Y. Pei, L. Ouahab and O. Kahn, *Adv. Mater.*, 1996, **8**, 60; J. P. Sutter, N. Daro, S. Golhen, L. Ouahab and O. Kahn, *Mol. Cryst. Liq. Cryst.*, in press.

2 D. Leznoff, C. Rancurel, J. P. Sutter, S. Golhen, L. Ouahab, S. J. Rettig and O. Kahn, *Mol. Cryst.*, *Liq. Cryst.* (in press); J. P. Sutter, M. L. Kahn, S. Golhen, L. Ouahab and O. Kahn *Chem. Eur. J.*, 1998, **4**, 571; J. P. Sutter, M. Fettouhi, L. Li, C. Michaut, L. Ouahab and O. Kahn, *Angew. Chem.*, *Int. Ed. Engl.*, 1996, **35**, 2113; Y. Pei, A. Lang, P. Bergerat, O. Kahn, M. Fettouhi and L. Ouahab, *Inorg. Chem.* 1996, **35**, 193.

3 C. Rancurel, J. P. Sutter, O. Kahn, P. Guionneau, G. Bravic and D. Chasseau, *New J. Chem.*, 1997, **21**, 275.

4 T. Akita, Y. Mazahiro, K. Kobayashi, N. Koga and H. Iwamura, *J. Org. Chem.*, 1995, **60**, 2092.

5 H. M. McConnel, *J. Chem. Phys.*, 1963, **39**, 1910; H. Iwamura, *Adv. Phys. Org. Chem.*, 1990, **26**, 179253.

6 M. Okumura, W. Mori and K. Yamaguchi, *Chem. Phys. Lett.*, 1994, **219**, 36; *Mol. Cryst. Liq. Cryst.*, 1993, **232**, 35.

7 G. A. Baker, Jr., G. S. Rushbrooke and H. E. Gilbert, *Phys. Rev. A*, 1964, **135**, 1272.

8 W. Strohmeier and K. Gerlach, *Chem. Ber.*, 1961, **94**, 398.

9 G. M. Sheldrick, SHELXS-86. Program for the Solution of Crystal Structures, University of Göttingen, Germany, 1990.

10 G. M. Sheldrick, SHELXL-97. Program for the Refinement of Crystal Structures, University of Göttingen, Germany, 1997.

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