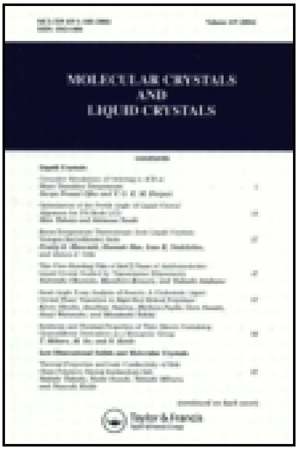

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Synthesis and Magnetic Behavior of Paramagnetic Phosphorus-Containing Ligands and their Metal Complexes

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Synthesis and Magnetic Behavior of Paramagnetic Phosphorus-Containing Ligands and their Metal Complexes

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The synthesis of new paramagnetic phosphorus-containing compounds, (*para*-RAD-phenyl)diphenylphosphine and phosphine oxide (RAD = nitronylnitroxide, ^{t}BuNO), is described. Complexation of these phosphines with diamagnetic metal centres yields, for example, intermolecular ferromagnetic interactions with {$Mo(CO)_5$(phosphine)}, antiferromagnetic interactions with {AuCl(phosphine)} and {$PdCl_2$(phosphine)$_2$}, a complex with multiple paramagnetic ligands. Ligation of nitronylnitroxide-containing phosphines to paramagnetic metals is hindered by catalytic nitrogen to phosphorus oxo-transfer to form the corresponding iminonitroxide-substituted phosphine oxide. A molecular square containing two nitronylnitroxide-substituted phosphine oxide ligands and two Mn(hfac)$_2$ units is also described.

Keywords: nitronyl nitroxide; phosphine; molecular magnetism

INTRODUCTION

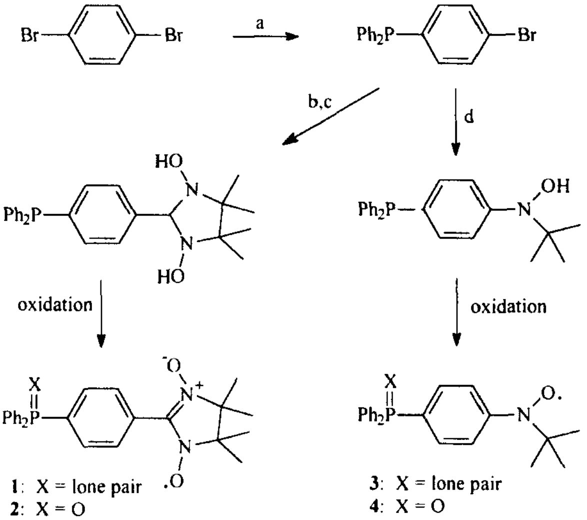
Nitroxide radicals are well-utilized building blocks in the synthesis of molecular materials. Purely organic materials, as well as metal complexes containing nitroxide units, are well known. However, the very weak basicity of the nitroxide functionality, which limits the coordination chemistry of the ligand, has led to the development of numerous nitroxides in which a strong co-ligand is incorporated.[1] The majority of such systems utilize hard nitrogen donors, especially planar N-heterocycles (e.g. pyridine, triazole) as co-ligands.[2] Phosphorus, the heavier congener of nitrogen, has a vast coordination chemistry of its own and yet phosphorus ligands have been notably absent in nitronylnitroxide and nitroxide chemistry. Phosphorus ligands, in particular phosphines, offer several differences compared with more traditional nitrogen donors: their ability to coordinate soft, low-valent metal centres, their pseudo-tetrahedral geometry and finally, access to the wealth of known coordination architectures involving phosphines. With these ideas in mind we have began the development of paramagnetic phosphines and phosphine oxides, their complexation to metal centres and the consequent examination of their magnetic properties. Some preliminary results in this area are reported in this contribution.

RESULTS AND DISCUSSION

Synthesis of Paramagnetic Phosphine and Phosphine Oxide Compounds.

The synthesis of radical-substituted triphenylphosphine and triphenylphosphine oxide compounds is shown in Scheme 1. Monolithiation of dibromobenzene followed by reaction with chlorodiphenylphosphine gives (*para*-diphenylphosphino) bromobenzene.[3] From this starting material, reaction with ^{n}BuLi, followed by DMF gives the *para*-substituted aldehyde, which is condensed with 2,3-dimethyl-2,3-dihydroxyaminobutane in standard fashion[4] to give the radical precursor of (*para*-nitronylnitroxide-phenyl) diphenylphosphine. Reaction of the same (*para*-diphenyl phosphino)bromobenzene with ^{n}BuLi, followed instead by ^{t}BuNO gives (*para*-^{t}BuNOH-phenyl)diphenylphosphine.[5] The final oxidation conditions of these radical precursors are important: oxidation using Ag_2O/CH_2Cl_2 yields the phosphine radicals **1** and **3**, while $NaIO_4$ oxidation under phase-transfer conditions yields the phosphine *oxide* radicals **2** and **4**.

The nitronylnitroxide-substituted compounds show the expected five-line ESR spectrum, without any coupling to the phosphorus atom. The ESR spectra of the ^{t}BuNO-substituted compounds show a three-line pattern with much fine structure; phosphorus coupling has been previously observed in this case.[5] All compounds presented here (except for **3**, which is prepared *in situ*) show antiferromagnetic coupling at low temperature in the solid state. Note that the (*ortho*-nitronylnitroxide-phenyl)diphenylphosphine oxide, prepared in a similar manner, exhibits *ferromagnetic* coupling at low temperature.[6]

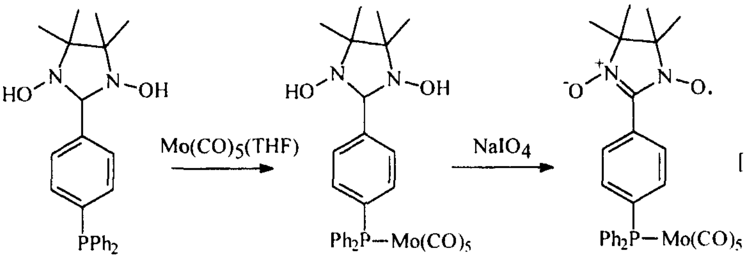


Scheme 1. (a) 1. ^{n}BuLi. 2. Ph_2PCl. (b) 1. ^{n}BuLi. 2. DMF. (c) 2,3-dimethyl-2,3-dihydroxyaminobutane. (d) 1. ^{n}BuLi. 2. ^{t}BuNO.

Paramagnetic Phosphine Complexes Containing Diamagnetic Metal Centres

Phosphine coordination chemistry encompasses a vast literature, containing a myriad of structural motifs. In particular, the ability of phosphine ligands to bind strongly to soft, low-valent metal centres allows for the use of such metal centres as platforms for the design of new magnetic materials. The diamagnetic metal centres used below act as an anchor in the construction of molecules in which the spin carriers are located not at the metal centre but around the periphery. Moreover, diamagnetic metal ions have been shown to transmit magnetic interactions between paramagnetic centres.[7] The metal centre thus controls the geometry and may influence the inter- and intramolecular interactions of the paramagnetic periphery.

Mo(0) Complex: The reaction of the radical precursor of **1** with {$Mo(CO)_5(THF)$} (generated *via* photolysis of $Mo(CO)_6$ in THF), followed by oxidation with $NaIO_4$ yields {$Mo(CO)_5(\mathbf{1})$}, **5** (Equation 1).



[1]

5

The X-ray structure of **5**, shown in Figure 1, confirms the expected octahedral geometry. The temperature dependence of the magnetic susceptibility for compound **5** was measured in the temperature range 2-300 K, with an applied field of 1000 Oe. The plot of $\chi_M T$ vs. T, where χ_M is the molar susceptibility corrected for core diamagnetism and T the temperature, (Figure 2) is indicative of intermolecular ferromagnetic interactions in the solid state at low temperature. Note that the $\chi_M T$ vs. T plot for the ligand, **1**, (Figure 2) shows *anti*ferromagnetic coupling. Hence, the Mo(CO)$_5$ fragment aligns the paramagnetic periphery to obtain a ferromagnetically coupled species.

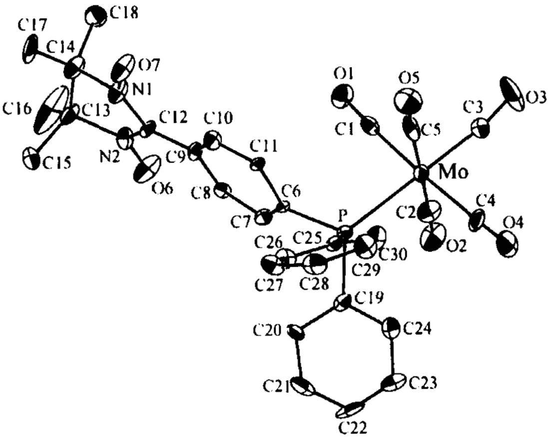


Figure 1. Molecular structure of {Mo(CO)$_5$(**1**)}, **5**. Selected bond lengths: Mo-P, 2.546(2) Å; N-O, 1.305(17) Å and 1.266(16) Å.

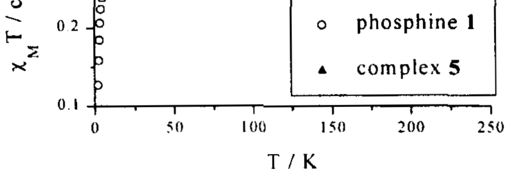
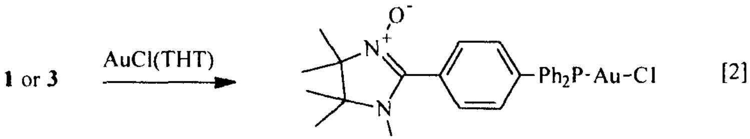


Figure 2. Experimental $\chi_M T$ vs. T curves for phosphine **1** and complex **5**.

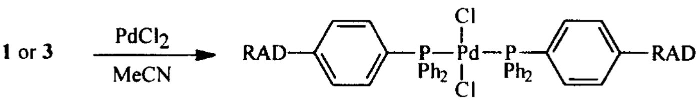
Au(I) Complexes: Monovalent gold is known to bind extremely strongly with phosphine ligands. A wide range of coordination geometries are supported, from linear (most common) to tetrahedral.[8] In addition, gold is known to form weakly attractive bonds with itself in the solid state known as aurophilic interactions.[9] A consequence of relativistic effects of gold atoms, this makes complexes of gold with the paramagnetic phosphines of particular interest. Reaction of the radical precursor of ligand **1** with AuCl(THT) (THT = C_4H_8S) followed by oxidation with Ag_2O gives in good yield {AuCl(**1**)}, **6**. The ligand can also be reacted directly with AuCl(THT) to give the identical product (Equation 2). Depending on the solvent, this compound crystallizes to form either green, **6**, or blue,**7**, crystals.



6: green crystals
7: blue crystals

The temperature dependence of χ_M for **6** indicates substantial antiferromagnetic interactions at low temperature as evidenced by a maximum in the curve at 3.5 K. The blue solid **7** shows weaker antiferromagnetic interactions. In the absence of structures, it is difficult to accurately interpret the source of such interactions, yet it is clear that the gold centre acts as a template for the arrangement of the peripheral nitronylnitroxide radicals in a novel fashion. The use of higher stoichiometries of phosphine and other anions to yield, for example $AuXP_2$, $AuXP_3$ and $[AuP_4]X$ species is currently under examination.

Pd(II) Complexes: The use of Pd(II) allows for the introduction of two paramagnetic phosphines onto the same metal centre, in a square planar environment. The reaction of $PdCl_2$ in acetonitrile with two equivalents of phosphines **1** or **3** yields {*trans*-$PdCl_2$(**1**)$_2$}, **8**, and {*trans*-$PdCl_2$(**3**)$_2$}, **9** (Equation 3).



[3]

8: RAD = nitronylnitroxide
9: RAD = ^{t}BuNO

The room temperature ESR spectra in solution of **8** and **9** (Figure 3) show nine-line (g = 2.006; a = 3.7 G) and five-line (g = 2.005; a = 6.1 G) patterns respectively, indicating electronic coupling to four equivalent (in **8**) and two equivalent (in **9**) nitrogen atoms. This coupling of the radicals to each other is likely through-space in origin.

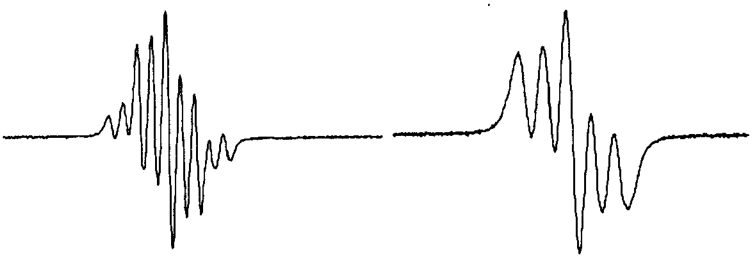


Figure 3. Solution ESR spectra (CH_2Cl_2) of Pd complexes **8** (left) and **9** (right).

The crystal structure of **9** is shown in Figure 4 and clearly illustrates two (*para*-^{t}BuNO-phenyl)diphenylphosphine ligands, **3**, bound in a *trans* fashion to the Pd(II) metal centre. The structure of **8** is assumed to be similar. For **8** at high temperature (50-300 K) $\chi_M T$ is equal to 0.69 cm^3 K mol^{-1}, consistent with two S=1/2 radicals. As the temperature is lowered from 50 to 2 K, $\chi_M T$ decreases to 0.52 cm^3 K mol^{-1}, consistent with antiferromagnetic coupling. This is likely a result of intermolecular interactions between nitronyl nitroxides on neighbouring molecules rather than intramolecular coupling.

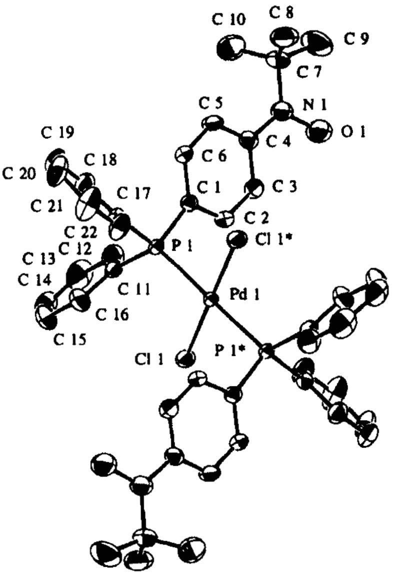


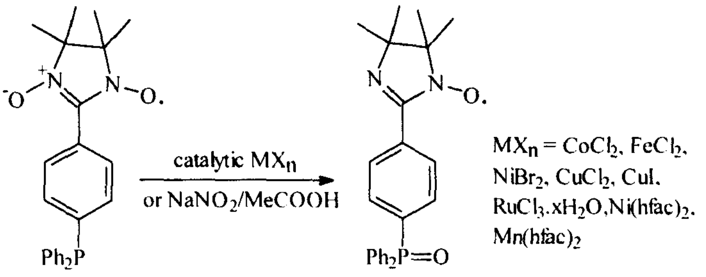
Figure 4. Molecular structure of {*trans*-$PdCl_2(\mathbf{3})_2$}, **9**. Selected bond lengths and angles: Pd-P, 2.3298(6); Pd-Cl, 2.2865(7); N-O, 1.286(3) Å; P-Pd-Cl, 92.15(2)°.

Complexes Containing Paramagnetic Metal Centres

Phosphine Complexes: The formation of metal-phosphine complexes in which both the metal and the phosphine are paramagnetic is an attractive goal in terms of studying novel magnetic materials and also for examining the question of how well phosphorus atoms mediate magnetic exchange. To this end, the reaction of MX_2 (M = Fe, Co, Ni; X = Cl, Br) and (*para*-nitronylnitroxide-phenyl)diphenylphosphine, **1**, was attempted. A powder of {$CoCl_2(\mathbf{1})_2$} was successfully isolated, with a value of $\chi_M T$ of 2.77 cm^3 K mol^{-1} at room temperature; this value decreased to 1.60 cm^3 K mol^{-1} at 2 K. Single crystals of this compound could not be obtained, however, due to a slow decomposition in solution (see below).

Although the cobalt-phosphine complex was isolable, the reactions of dark blue **1** with Ni(II) yielded only an orange solution and precipitated metal salts. Attempts to recrystallize the aforementioned cobalt complex resulted in the isolation of $CoCl_2$ and an orange solid. This was unambiguously identified as (*para*-iminonitroxide-phenyl)diphenylphosphine*oxide*, **10**, *i.e.* the product of oxo-transfer from the nitronylnitroxide moiety to the phosphine (Equation 4). Attempts to synthesize (*para*-iminonitroxide-phenyl)diphenylphosphine (*i.e.* without phosphine oxide formation) *via* SeO_2 catalysis[10] or HCl dehydration of precursor material or by $NaNO_2$/acetic acid treatment of phosphine **1** yielded consistently the phosphine oxide product **10**. These standard reactions, which convert nitronylnitroxides to iminonitroxides by selective removal of one oxygen, in this case also oxidize the phosphine to the corresponding phosphine oxide. In the solid state compound **10** shows weak antiferromagnetic interactions at low temperatures.

This oxo-transfer reaction effectively negates the possibility of forming complexes of **1** with paramagnetic metal centres (which have active redox chemistry, allowing for the oxo-transfer to occur). In fact, the reaction is catalytic in metal: 5 mol% of MX_2 is sufficient to effectively convert **1** to **10** in high yields. Cu(I), Ru(III), Fe(II), Fe(III) and Mn(II) also effect this reaction. Reactions with ligand **3**, which may be more stable with respect to oxo-transfer, are in progress.



1 **10**

[4]

Phosphine Oxide Complexes: Nitroxide-containing phosphine oxide molecules can act as ligands either through the N-O (nitroxide) or the P=O group. As both are weak ligands, highly Lewis acidic metal centres are preferred for complex formation. Accordingly, reaction of Mn(hfac)$_2$ (hfac = hexafluoroacetylacetonate) with (*para*-nitronylnitroxide-phenyl)diphenyl phosphine oxide, **2**, yielded {Mn(hfac)$_2$(**2**)}, **11**, whose structure is shown in Figure 5.

The X-ray structure reveals a molecular square, composed of two Mn(hfac)$_2$ units and two phosphine oxide ligands. Each ligand **2** is bridging two Mn centres, by virtue of N-O bonding to one Mn and P=O bonding to the other. The octahedral coordination of Mn is distorted with Mn-O distances ranging from 2.078(4) to 2.177(4) Å with the shortest length corresponding to the PO-Mn bond.

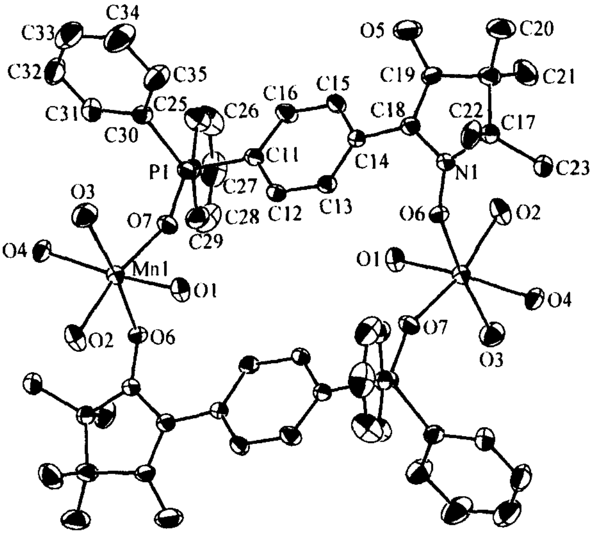


Figure 5. Molecular structure of {Mn(hfac)$_2$(**2**)}, **11**. Hfac ligands have been removed for clarity.

The temperature dependence of the magnetic susceptibility for **11** showed that at 300 K $\chi_M T$ is equal to 6.5 cm^3 K mol^{-1}, a much lower value than that expected for non-interacting species (9.5 for $2*S_{Mn} = 5/2$ and $2*S_{Rad} = 1/2$). A strongly antiferromagnetically coupled system is hence present. As the temperature is lowered $\chi_M T$ decreases to reach a plateau value of 6 cm^3 K mol^{-1} between 150 K and 20 K corresponding to two sets of S = 2 states. Thus, magnetic and structural results indicate this complex could be considered as being constituted of two isolated dimers. Each dimer contains two sets of $S_{Mn} = 5/2$ and $S_{Rad} = 1/2$ spins interacting directly through the NO-Mn bond. Any interactions that may occur between these strongly coupled dimers through the PO-Mn bond are negligibly small.

CONCLUSIONS

Novel paramagnetic phosphorus-containing nitroxide and nitronylnitroxide ligands have been prepared. Their complexation with diamagnetic transition metals illustrates the concept of using such metals as platforms for the construction of high spin molecules where the spins are located at the periphery of the molecule. The catalytic oxo-transfer reaction of nitronylnitroxide-containing phosphines with some metals, notably paramagnetic ones, rendered some metal complexes unstable. A molecular square containing two $Mn(hfac)_2$ units bridged by two (*para*-nitronyl nitroxide-phenyl)diphenylphosphine oxide was also characterized. Extensions of this work to complexes bearing multiple paramagnetic ligands, and more importantly, to ligands which themselves incorporate multiple radicals (and their metal complexes) towards the design of 2D and 3D molecular magnetic materials are envisioned.

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