Ruthenium(II) complexes of a 2,2′-biphosphinine

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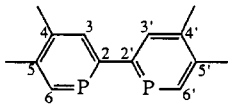
Abstract

The biphosphinine complexes $[RuCl_2(dmso)_2(bp)]$ (**2**) and *cis*-$[RuCl_2(bp)_2]$ (**3**) (bp = 4,4′,5,5′-tetramethyl-2,2′-biphosphinine) have been prepared from $[RuCl_2(dmso)_4]$ and the free ligand. The crystal and molecular structure of **2**, which crystallised in the space group $C2/c$ with $a = 17.329(1)$, $b = 16.008(1)$, $c = 18.733(2)$ Å, $\beta = 104.75(1)°$, $V = 5025.2(1.4)$ Å^3 and $Z = 8$ and refined to $R = 0.042$, $R_w = 0.089$, is presented and NMR data pertaining to both complexes is discussed. Analyses of the complexes suggest that the biphosphinine serves as a good π-acceptor ligand towards the ruthenium(II) centres.

Introduction

Delocalised nitrogen containing aromatic ligands are associated with many electrochemical and photochemical processes, because their low-lying π^* orbitals are effective acceptors of electrons from excited metal centres [1]. Amongst these ligands, 2,2′-bipyridine (bipy) has been shown to be particularly efficient in a number of catalytic processes, including the photolysis of water [2].



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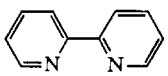
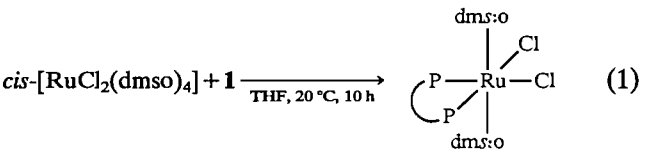


bipy

We have recently synthesised a 2,2′-biphosphinine, **1** [3, 4], whose properties are potentially quite interesting when viewed against this background. The electronegativity of sp^2 phosphorus is lower than that of nitrogen**, which suggests a less polarised ligand π system than would be found in a corresponding bipyridine. Additionally, a more efficient overlap of the phosphorus 3p orbital with the carbocyclic π system implies a more 'aromatic' acceptor orbital for metal to ligand charge transfers than is available in the aza analogue. An electrochemical study has recently confirmed these hypotheses, and demonstrated that the π^* LUMO of a biphosphinine ligand lies at least 0.35 V below that of the corresponding bipyridine [4].

The study of bipyridine ligands has focussed most sharply upon complexes of ruthenium(II), because of favourable redox potentials and excited state lifetimes which have made them particularly active mediators in photoinduced electron-transfer processes [1]. Therefore, it seemed logical to initiate a study of the coordination of biphosphinines to $[RuCl_2]$ centres, both to facilitate comparisons with their bipyridine analogues and to lay the foundations for a systematic study of the ruthenium–biphosphinine system.

In this paper, we present some preliminary results concerning the interactions of 4,4′,5,5′-tetramethyl-2,2′-biphosphinine (bp) with dichloro tetrakis(dimethyl sulfoxide)ruthenium(II), which have led to the isolation and identification of the complexes $[RuCl_2(dmso)_2(bp)]$ (**2**) (eqn. (1)) and *cis*-$[RuCl_2(bp)_2]$ (**3**) (eqn. (2)).



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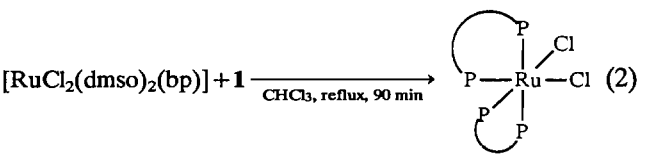

(2)

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**According to a recent MCD study [5], the phosphorus atom in phosphabenzene is slightly more π-electronegative than carbon.

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Experimental

Reactions were performed under an atmosphere of nitrogen using standard Schlenk techniques, and solvents were distilled from phosphorus pentoxide (hexane and sym-tetrachloroethane) or sodium benzophenone ketyl (tetrahydrofuran) prior to use. The compounds 4,4',5,5'-tetramethyl-2,2'-biphosphinine (**1**) [3, 4] and *cis*-dichloro tetrakis(dimethyl sulfoxide)ruthenium(II) [6] were prepared as described previously.

Spectroscopic determinations were performed on Bruker AC 200 SY or AC 400 SY Fourier transform instruments operating at 200.13 MHz for ^{1}H, 50.32 or 100.64 MHz for ^{13}C, and 81.01 MHz for ^{31}P. Coupling constants are given in hertz. Chemical shifts, in parts per million with positive values appearing to high frequency of the reference, are quoted relative to external TMS or H_3PO_4 as appropriate. Microanalyses were performed by the 'Service de Microanalyses du CNRS' at Gif-sur-Yvette, France.

Preparation of [$RuCl_2(dmso)_2(bp)$] (2)

Biphosphinine **1** (150.0 mg, 6.10×10^{-4} m) was added to a tetrahydrofuran (10 ml) solution of *cis*-[$RuCl_2(dmso)_4$] (286.0 mg, 5.88×10^{-4} m), and the mixture was stirred for 12 h. After filtration through celite, and slow evaporation of solvent in a stream of nitrogen, orange crystals of [$RuCl_2(dmso)_2(bp)$] (**2**) were deposited. These were washed with pentane (2×5 ml) and dried *in vacuo*.

2: yellow–orange crystals; yield 172 mg, 51%. *Anal.* Calc. for: $C_{18}H_{28}Cl_2O_2P_2RuS_2\cdot\frac{1}{2}$THF: C, 39.34; H, 5.28. Found: C, 40.06; H, 5.30%.

^{31}P NMR ($C_2D_2Cl_4$): δ 209.3 ppm.

^{1}H NMR ($C_2D_2Cl_4$): δ 1.86 (m, 2H, THF), 2.44 (d, J(PH) = 16, 6H, Me), 2.51 (s, 6H, Me), 3.24 (s, 12H, dmso), 3.76 (m, 2H, THF), 8.14 (d, ^{3}J(PH) = 22, 1H, H-3), 8.62 (d, ^{2}J(PH) = 20, 1H, H-6) ppm.

^{13}C NMR ($C_2D_2Cl_4$): 22.8 (d, J(PC) = 3, Me), 24.5 (d, J(PC) = 11, Me), 27.4 (s, THF), 45.3 (s, dmso), 68.0 (s, THF), 131.8 (dd, J(PC) = 28, 10, C-3), 136.1 (d, J(PC) = 29, C-4), 139.4 (d, J(PC) = 26, C-6), 148.5 (dd, J(PC) = 16, 3, C-5), 152.7 (dd, J(PC) = 44, 31, C-2) ppm.

Preparation of cis-[$RuCl_2(bp)_2$] (3)

Biphosphinine **1** (50.4 mg, 2.05×10^{-4} m) was added to a chloroform (1 ml) solution of *cis*-[$RuCl_2(dmso)_4$] (30.1 mg, 6.09×10^{-5} m), and the mixture was refluxed for 90 min. The orange crystals of *cis*-[$RuCl_2(bp)_2$] (**3**) which were deposited were washed with chloroform (2×0.3 ml) and pentane (1 ml) and dried *in vacuo*.

3: orange crystals; yield 32.1 mg, 74%. *Anal.* Calc. for: $C_{28}H_{32}Cl_2P_4Ru\cdot\frac{1}{2}CHCl_3$: C, 47.27; H, 4.52. Found: C, 46.91; H, 4.81%.

^{31}P NMR ($C_2D_2Cl_4$): δ 198.8, 205.4 (see below).

^{1}H NMR ($C_2D_2Cl_4$): δ 2.19 (s, 3H, Me), 2.31 (s, 3H, Me), 2.54 (s, 3H, Me), 2.59 (s, 3H, Me), 7.42 (m, ΣJ(PH) = 19.9, 1H, H-3, ring *cis* to P), 8.11 (m, ΣJ(PH) = 22.2, 1H, H-6, ring *cis* to P), 8.25 (m, ΣJ(PH) = 19.9, 1H, H-3, ring *trans* to P), 8.89 (m, ΣJ(PH) = 19.7, 1H, H-6, ring *trans* to P) ppm.

^{13}C NMR ($C_2D_2Cl_4$): δ 23.2 (s, Me), 23.8 (s, Me), 24.9 (s, Me), 25.2 (s, Me), 131.9 (s, C-3), 132.6 (s, C-3), 136.1 (ψt, ΣJ(PC) = 27, C-4), 138.6 (ψt, ΣJ(PC) = 26, C-4), 141.4 (ψt, ΣJ(PC) = 26, C-6), 141.9 (ψt, ΣJ(PC) = 31, C-6), 148.9 (m, C-5), 149.1 (m, C-5), 153.5 (m, C-2), 154.0 (m, C-2) ppm.

Simulation of the ^{31}P NMR spectrum of 3

This was performed using the PANIC program on a 80.1 MHz spectrum which had a digital resolution of 0.2 Hz, and in which the combination bands were clearly visible (see Fig. 2). Confirmation of the sensitivity of the spectrum to individual couplings was obtained by variation of each parameter, prior to a simultaneous iteration of all variables which converged to within 0.4 Hz of every experimentally observed transition. The values: $\delta_{P(A)}$, 205.4; $\delta_{P(B)}$, 198.8 ppm; $J_{(A,\,A')}$, 461.6; $J_{(A,\,B)}$, −4.1; $J_{(A,\,B')}$, −46.4; $J_{(B,\,B')}$, −48.4 Hz were obtained from the final iteration.

X-ray structure determination for 2

Crystals of **2**, $C_{18}H_{28}Cl_2RuO_2P_2S_2\cdot\frac{1}{2}$THF, were grown by slow cooling of a THF solution of the compound. Data were collected at -150 ± 0.5 °C on an Enraf Nonius CAD4 diffractometer. The crystal structure was solved and refined using the Enraf Nonius SDP package. The compound crystallises in space group $C2/c$, $a = 17.329(1)$, $b = 16.008(1)$, $c = 18.733(2)$ Å, $\beta = 104.75(1)°$; $V = 5025.2(1.4)$ Å^3; $Z = 8$; $D_{calc} = 1.709$ g/cm^3; Mo Kα radiation ($\lambda = 0.71073$ Å) graphite monochromator; $\mu = 11.4$ cm^{-1}; F(000) = 2656. A total of 7561 unique reflexions was recorded in the range $2 \leqslant 2\theta \leqslant 60°$ of which 1720 with $F^2 < 3.0\sigma(F^2)$ were considered as unobserved, leaving 5841 for solution refinement. The structure was solved by Patterson methods. A final difference Fourier map revealed the existence of a highly disordered THF molecule, whose disorder is not fully understood at the present stage of refinement. The hydrogen atoms were included as fixed contributions in the final stages of least-squares refinement while using anisotropic temperature factors for all other atoms. A non-Poisson weighting scheme was applied with a p factor of 0.06. The final agreement factors were $R = 0.042$, $R_\omega = 0.089$, $GOF = 1.85$.

Results

X-ray crystallographic study

Crystals of **3** suitable for X-ray crystallographic studies have not been obtained to date. A structural study of **2**, to evaluate the effects of coordination upon the biphosphinine ligand and the metal coordination sphere, was therefore undertaken.

The structural determination, depicted in Fig. 1, and detailed in Table 1, confirms a chelating mode for the biphosphinine ligand. The Ru, P(1), P(12), C(6) and C(7) atoms are strictly coplanar, with only a very slight (3°) deviation from planarity being observed for the remainder of the aromatic system. The most significant modification of the geometry of the biphosphinine upon coordination is revealed by the internal CPC angles, which open from 100.2(2)° in the free ligand [4] to 106.0(2)° in the complex. This reflects a simple rehybridisation of the biphosphinine lone pairs, and is mirrored by corresponding decreases in the mean adjacent CCP angles, whilst leaving the remainder of the ligand unchanged. Most notably, the significant difference of −0.020 Å between the PC(2) and PC(6) distances which is observed in the free ligand [4] is retained in the complex (−0.029 Å).

A dissymmetry within the immediate coordination sphere of the ruthenium atom complicates the interpretation of the major internuclear separations. Nonetheless, the Ru–P distances of **2** (2.2353(8) and 2.2428(7) Å) lie between the values found for PF_3 ligands in $[RuCl_2(PF_3)_2(PPh_3)_2]$ (2.170(2) Å) [7] and those of more classical triorganylphosphane ligands (2.292 to 2.433 Å) [8], and are clearly very short, reflecting the high s-electron density of the biphosphinine hybrid donor orbitals. Consistently the RuCl separations (2.4286(8) and 2.4060(8) Å) reflect the low *trans* influence of the biphosphinine, and are also short when compared to those found *trans* to more normal phosphane ligands; they more closely resemble separations *trans* to much weaker donors such as 1,5-cyclooctadiene [9] (see Table 2). Finally, the mutually *trans* RuS distances of 2.3346(8) and 2.3444(8) Å lie closer to the mean values found for dmso *trans* to sulfur in the Ru(III) complexes $[Ru(dmso)_3Cl_3]$ (2.341(2) Å) and $[Ru(dmso)_2Cl_4]^-$ (2.348(1) Å) [11] than to their Ru(II) analogues $[Ru(dmso)_4X_2]$ (X = Cl, 2.352(2),

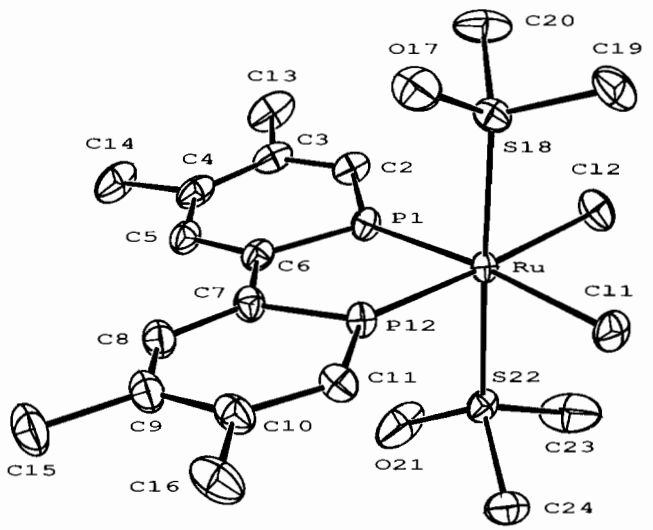


Fig. 1. The molecular structure of $[RuCl_2(dmso)_2bp]$ (**2**).

TABLE 1. Bond lengths (Å) and angles (°) for $[RuCl_2(dmso)_2(bp)]$ (**2**)

Distances			
Ru–Cl1	2.4060(8)	C7–C8	1.401(4)
Ru–Cl2	2.4286(8)	C7–P12	1.723(3)
Ru–P1	2.2353(8)	C8–C9	1.404(5)
Ru–P12	2.2428(7)	C9–C10	1.408(5)
Ru–S18	2.3346(8)	C9–C15	1.518(4)
Ru–S22	2.3444(8)	C10–C11	1.395(4)
P1–C2	1.708(3)	C10–C16	1.515(5)
P1–C6	1.718(3)	C11–P12	1.695(3)
C2–C3	1.397(5)	O17–S18	1.484(3)
C3–C4	1.400(5)	S18–C19	1.770(4)
C3–C13	1.520(5)	S18–C20	1.767(4)
C4–C5	1.403(5)	O21–S22	1.479(3)
C4–C14	1.525(5)	S22–C23	1.786(4)
C5–C6	1.399(4)	S22–C24	1.783(4)
C6–C7	1.467(4)		
Angles			
Cl1–Ru–Cl2	90.94(3)	C5–C6–C7	124.8(3)
Cl1–Ru–P1	172.56(3)	C6–C7–C8	125.8(3)
Cl1–Ru–P12	92.53(3)	C6–C7–P12	113.9(2)
Cl1–Ru–S18	89.56(3)	C8–C7–P12	120.2(2)
Cl1–Ru–S22	89.10(3)	C7–C8–C9	124.7(3)
Cl2–Ru–P1	96.42(3)	C8–C9–C10	123.6(3)
Cl2–Ru–P12	176.30(3)	C8–C9–C15	116.8(3)
Cl2–Ru–S18	86.70(3)	C10–C9–C15	119.7(3)
Cl2–Ru–S22	91.78(3)	C9–C10–C11	122.1(3)
P1–Ru–P12	80.13(3)	C9–C10–C16	120.5(3)
P1–Ru–S18	91.94(3)	C11–C10–C16	117.4(3)
P1–Ru–S22	89.58(3)	C10–C11–P12	123.4(3)
P12–Ru–S18	92.05(3)	Ru–P12–C7	115.5(1)
P12–Ru–S22	89.54(3)	Ru–P12–C11	138.5(1)
S18–Ru–S22	177.97(3)	C7–P12–C11	106.0(1)
Ru–P1–C2	138.5(1)	Ru–S18–O17	117.2(1)
Ru–P1–C6	115.5(1)	Ru–S18–C19	112.0(1)
C2–P1–C6	106.0(2)	Ru–S18–C20	112.6(1)
P1–C2–C3	122.4(3)	O17–S18–C19	107.4(2)
C2–C3–C4	122.8(3)	O17–S18–C20	105.9(2)
C2–C3–C13	117.9(3)	C19–S18–C20	100.3(2)
C4–C3–C13	119.3(3)	Ru–S22–O21	116.0(1)
C3–C4–C5	123.7(3)	Ru–S22–C23	113.0(2)
C3–C4–C14	120.5(3)	Ru–S22–C24	112.7(1)
C5–C4–C14	115.8(3)	O21–S22–C23	108.8(3)
C4–C5–C6	124.3(3)	O21–S22–C24	105.7(2)
P1–C6–C5	120.6(2)	C23–S22–C24	99.1(2)
P1–C6–C7	114.6(2)		

Numbers in parentheses are e.s.d.s in the least significant digits.

TABLE 2. A comparison of ruthenium chlorine bond lengths in selected Ru(II) complexes

Ru(II)–Cl bond lengths (Å)	*trans* to	Complex	Reference
2.395(6)	COD	*cis*-[Ru(COD)(CO)(MeCN)Cl_2]	9a
2.4286(8) 2.4060(8)	P	**2**	
2.428(6)	CO	[Ru(*p*-ClC_6H_4–NC)(CO)(PPh_3)$_2Cl_2$]	9b
2.446(2)	P	*cis*-[$RuCl_2$dppm$_2$]	8a
2.460(6)	NC:	[Ru(*p*-ClC_6H_4–NC)(CO)(PPh_3)$_2Cl_2$]	9b
2.461(3)	P	*trans*-[Ru(PPh_3)$_3Cl_2$CO]	10a
2.469(2)	P	[Ru(*o*-C_6H_4(PPh_2)$_2$)(dmso)Cl_2CO]	8b

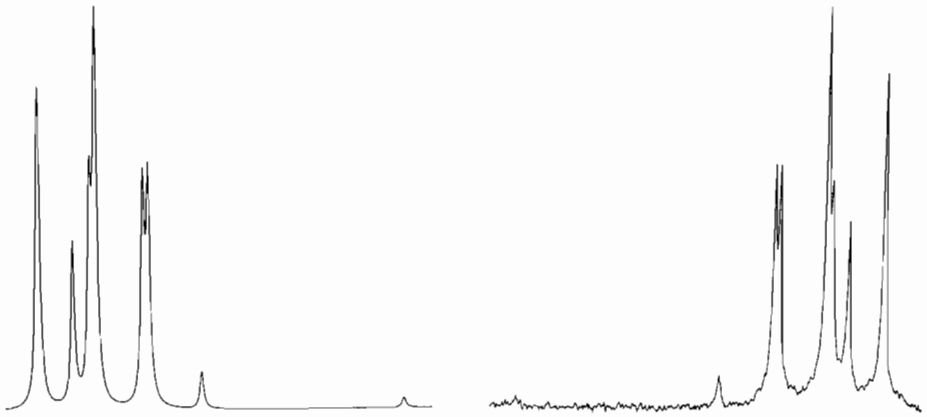


Fig. 2. A comparison of the calculated (high frequency) and observed (low frequency) components in the $^{31}P\{^1H\}$ NMR spectra of *cis*-[$RuCl_2$(bp)$_2$] (**3**).

Br 2.360(1) Å) [12]. Although there is some evidence for steric hindrance in the reference compounds, this further suggests that the biphosphinine ligand supplies very little electron density to the metal centre.

NMR spectroscopic studies

The $^{31}P\{^1H\}$ NMR spectrum of **3** has been successfully modelled as an $[AB]_2$ spin system, which confirms that the complex adopts a *cis* configuration in solution, and is not fluxional or dissociating on the NMR time scale (Fig. 2). The ^2J(PP) (*trans*) 461 Hz and ^2J(PP) (*cis*)-46 Hz coupling constants, which relate phosphorus atoms in the two different biphosphinine ligands, are both greater by a factor of *c.* 1.5 times than the corresponding values found in more classical *cis*-triorganylphosphane-ruthenium dichloride complexes [13]. This clearly reflects the anticipated increase in s-electron character in the ruthenium–biphosphinine hybrid orbitals upon going from formal sp^3 hybridisation of classical phosphanes to the sp^2 donors of the biphosphinine. Nonetheless, the value of ^2J(PP)(*cis*) is significantly smaller than the 69 Hz coupling between the *cis*-disposed PF_3 ligands in [Ru(PPh_3)$_2$(PF_3)$_2Cl_2$] [14]. Thus, even though the high positive charge on the donor atom may increase penetration of the P nucleus by the bonding s-electrons and induce a deceptively high s-character for the PF_3 ligand [15], the biphosphinine appears most likely to have a donor character intermediate between those of classical phosphanes and PF_3.

The difference between the large intercyclic and small intracyclic ^2J(PP)(*cis*) couplings in [$RuCl_2$(bp)$_2$] (−46 and −4 Hz, respectively) indicates a modest positive value of approximately 40 Hz for the three bond phosphorus–phosphorus coupling through the carbon backbone of the biphosphinine. The data given in refs. 13a and 16 suggest only +19 Hz for the analogous coupling through the dppe ligand skeleton in *trans*-[Ru(dppe)($PMePh_2$)$_2Cl_2$], thus tending to support the existence of a weak delocalised intercyclic communication through the bridge of the biphosphinine ligand. Significant PC2′, PC3′ and PC5′ couplings (31, 10 and 3 Hz, respectively) in the ^{13}C NMR spectrum of **2**, also imply small electronic interactions between the two halves of the biphosphinine. However, whilst there may be some electronic transfers through the bridge, the upfield coordination chemical shifts for the bridging carbon atoms of **2** are almost identical to those of the corresponding non-bridging C(6) atoms (17.9 and 15.5 ppm, respectively) and it seems probable that the charge density acquired by the phosphorus upon coordination

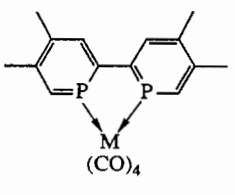
is not localised particularly in the region of C(2) and C(2').

Discussion

Our principal interest at the outset of this work lay in the potential π-acceptor character of the biphosphinine ligand. Several theoretical and experimental studies have established that for complexes of the general type $[RuCl_2(L)_2(L')_2]$, where the ligands are not sterically demanding, the more powerful π-acceptor ligands occupy positions *trans* to the chloride atoms [10]. This serves to reduce competition for electron density in the filled metal d orbitals, occasionally at the cost of a small increase in steric interactions.

From the structure of $[RuCl_2(dmso)_2(bp)]$ (**2**), it is clear that the biphosphinine, which adopts a position *trans* to chloride, must be a better acceptor than the dmso ligands. Additionally, although dmso is generally relatively difficult to displace from complexes of the general formula $[RuCl_2(dmso)_2(L)_2]$ (L=CO, ½ bipy) [6], we find that the preparation of **2** is rather difficult, because of a competitive formation of **3** from biphosphinine and the first-formed **2**. As there are no unusually short internuclear contacts in **2**, this cannot be a steric effect. Additionally, it is clear from the above discussion that the biphosphinine is unlikely to compete strongly with dmso as a σ donor. We can, therefore, suggest that the lability of **2** is good evidence that the majority of the metal d-electron density which is normally available for backbonding into the dmso is delocalised into the biphosphinine.

From this initial study, we feel justified in our initial assumption that the biphosphinine is a more efficient acceptor ligand than bipyridine. To date, except for a variety of complexes of $[M(CO)_4]$ (**4**) (M=Cr, Mo) [3, 4], no coordination chemistry of biphosphinines has been reported, and the only well characterised example (**5**) of any phosphinine nucleus bound to a metal in a high oxidation state proved to be too sensitive to be isolated [17].



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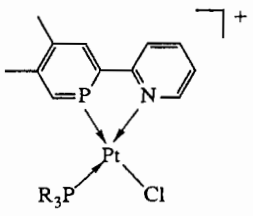

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In view of the respectable stabilities of **2** and **3**, which can be stored in air for appreciable periods, we nevertheless feel that further studies in this area will be fruitful. Investigations of the chemistry of a variety of metals towards **1** are in progress.

Acknowledgement

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