Complexes of Palladium(II) and Platinum(II) Thiocyanates with some Bidentate Amine, Phosphine, Arsine, Sulphide, and Selenide Ligands

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The bidentate ligands $CH_2(PPh_2)_2$, $CH_2(PPh_2S)_2$, $CH_2(PPh_2Se)_2$, and $CH_2(AsPh_2S)_2$ all form thiocyanato-*S* complexes $[M(L–L)(SCN)_2]$ (L–L = bidentate ligand, M = Pd or Pt) with palladium(II) and platinum(II) thiocyanates. Reactions of 1,2-bis(diphenylphosphino)ethane with $K_2[Pd(SCN)_4]$ yield, in addition to the previously reported $[Pd(Ph_2PC_2H_4PPh_2)_2][Pd(SCN)_4]$ and $[Pd(Ph_2PC_2H_4PPh_2)(NCS)(SCN)]$, a salt $[Pd(Ph_2PC_2H_4PPh_2)_2][CNS]_2$ and probably also a thiocyanato-*N* complex $[Pd(Ph_2PC_2H_4PPh_2)(NCS)_2]$; corresponding reactions with $K_2[Pt(SCN)_4]$ yield only the salts $[Pt(Ph_2PC_2H_4PPh_2)_2][Pt(SCN)_4]$ and $[Pt(Ph_2PC_2H_4PPh_2)_2][CNS]_2$, with no evidence for the formation of neutral mixed-ligand complexes $[Pt(Ph_2PC_2H_4PPh_2)(CNS)_2]$. Bis(diphenylarsino)methane forms a neutral 1 : 2 palladium complex $[Pd\{CH_2(AsPh_2)_2\}_2(SCN)_2]$ which appears to have a monomeric octahedral structure in the solid; with platinum(II) thiocyanate the products are four-co-ordinate $[Pt\{CH_2(AsPh_2)_2\}(NCS)(SCN)]$ and $[Pt\{CH_2(AsPh_2)_2\}_2][CNS]_2$. Unlike 2,2′-bipyridyl, which forms thiocyanato-*N* complexes, di-2-pyridylamine and di-2-pyridyl ketone form thiocyanato-*S* complexes with both palladium(II) and platinum(II) thiocyanates at room temperature: this behaviour is consistent with the less complete conjugation and greater steric requirements of the amine and ketone ligands.

THE electronic and steric factors which influence the metal–thiocyanate linkage, M–NCS or M–SCN, in palladium(II) and platinum(II) thiocyanate complexes $[ML_2(CNS)_2]$ (M = Pd or Pt) * have been discussed by many authors (see, for example, refs. 1—12). In purely

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* Thiocyanate is represented as CNS where it would be inappropriate, or is not possible, to specify the metal–thiocyanate linkage.

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electronic terms, we expect complexes with class ' a ' or weak class ' b ' ligands,[13] L, to contain *S*-bonded thiocyanate whereas with the stronger class ' b ' ligands the more ionic thiocyanato-*N* linkage will be preferred. However, the steric requirements of the linear M–NCS and bent M–SCN configurations are very different and in many cases may lead to the formation of the electronically less favoured isomer. Examples are known of complexes containing one *S*- and one *N*-bonded thiocyanate ligand [5-9] and the thiocyanate orientation may also be dependent on solvent [10,11] or temperature.[2,12]

TABLE 1

Analytical data for palladium and platinum thiocyanato-complexes

Complex	Analysis (%) Found C	H	N	Calc. C	H	N	M.p. (θ_c/°C)	Colour
$[Pt\{CH_2(PPh_2)_2\}(SCN)_2]$	46.0	3.2	3.9	46.6	3.2	4.0	138	Pale orange
$[Pd\{CH_2(PPh_2S)_2\}(SCN)_2]$	48.1	3.3	4.0	48.4	3.3	4.2	193	Orange
$[Pt\{CH_2(PPh_2S)_2\}(SCN)_2]$	42.7	2.9	3.6	42.7	2.9	3.7	210	Yellow
$[Pd\{CH_2(PPh_2Se)_2\}(SCN)_2]$	42.6	3.2	3.9	42.3	2.9	3.7	200	Brown
$[Pt\{CH_2(PPh_2Se)_2\}(SCN)_2]$	38.2	2.7	3.4	38.0	2.6	3.3	decomp.	Yellow
$[Pd\{CH_2(AsPh_2S)_2\}(SCN)_2]$	43.1	2.9	3.9	42.7	2.9	3.7	200	Orange
$[Pt\{CH_2(AsPh_2S)_2\}(SCN)_2]$	38.3	2.6	3.0	38.3	2.6	3.3	235	Yellow
$[Pd(Ph_2PC_2H_4PPh_2)_2][CNS]_2$	63.5	4.8	2.7	63.6	4.7	2.7	decomp.	White
$[Pt(Ph_2PC_2H_4PPh_2)_2][CNS]_2$	58.1	4.4	2.4	58.5	4.4	2.5	decomp.	White
$[Pt(Ph_2PC_2H_4PPh_2)_2][Pt(SCN)_4]$	47.8	3.4	4.1	47.4	3.4	4.0	decomp.	Pale yellow
$[Pd\{CH_2(AsPh_2)_2\}_2(SCN)_2]$	53.5	4.0	2.5	53.4	3.8	2.4	179	Orange-yellow
$[Pt\{CH_2(AsPh_2)_2\}(NCS)(SCN)]$	42.0	2.6	3.5	41.4	2.8	3.6	125	Pale yellow
$[Pd\{(C_5H_4N)_2NH\}(SCN)_2]$	36.0	2.3	17.6	36.6	2.3	17.8	215	Orange
$[Pt\{(C_5H_4N)_2NH\}(SCN)_2]$	30.0	2.1	15.0	29.9	1.9	14.5	200	Orange-yellow
$[Pd\{(C_5H_4N)_2CO\}(SCN)_2]$	38.2	2.3	13.5	38.5	2.0	13.8	130	Red-brown

Given that the radii of square-planar Pd^{II} and Pt^{II} are equal, to within 0.02 Å, steric effects in corresponding palladium and platinum complexes with the same ligand L will be virtually identical. Any differences in the metal–thiocyanate linkages may thus be attributed to variations in the electronic requirements of the two metals. Obviously, valid comparisons can only be made between palladium and platinum complexes having the same *cis* or *trans* square-planar geometry, but the majority of complexes reported in the literature involve unidentate ligands and in many cases the stereochemistry has not been unambiguously determined. We have now prepared parallel series of palladium(II) and platinum(II) thiocyanate complexes with some representative bidentate (*i.e.* potentially *cis* chelate) *N*-donor [2,2'-bipyridyl; di-2-pyridylamine, $(C_5H_4N)_2NH$; di-2-pyridyl ketone, $(C_5H_4N)_2CO$], *P*-donor [1,2-bis-(diphenylphosphino)ethane, $Ph_2PC_2H_4PPh_2$; bis(diphenylphosphino)methane, $CH_2(PPh_2)_2$], *As*-donor [bis-(diphenylarsino)methane, $CH_2(AsPh_2)_2$], and *S*- and *Se*-donor ligands [$CH_2(PPh_2S)_2$; $CH_2(AsPh_2S)_2$, $CH_2(PPh_2Se)_2$].

RESULTS

Physical data for new complexes are given in Table 1.

Identification of the Metal–Thiocyanate Linkage.—The frequency of the thiocyanate ν_3(C–S stretching) vibration distinguishes reliably between M–NCS and M–SCN,[5,14] but in most mixed-ligand complexes the relevant frequency region is obscured by ligand absorptions. The C–N stretching frequency is less trustworthy, but the i.r. *intensity* of the C–N stretching absorption differs significantly in the two types of compound, being at least 300% greater for *N*- than for *S*-bonded thiocyanate.[7,14,15] The C–N stretching bands in M–SCN compounds are typically rather sharp, with bandwidths at half-peak height ($\nu_{\frac{1}{2}}$) between 6 and 18 cm^{-1}, whereas the corresponding bands in M–NCS compounds are much broader, with ν- = 25—50 cm^{-1}.[7,14,15]

A number of our complexes were too insoluble to permit intensity measurements to be made in solution. To avoid complications arising from solvent effects and comparisons of solid and solution spectra, we have therefore limited our attention to the solid complexes. Miezis [16] has shown that integrated intensities of C–N stretching absorptions may be measured with an error of ±10% in carefully prepared KBr discs: given the 300% difference between *S*- and *N*-bonded thiocyanate, errors of this order are quite acceptable. Bailey *et al.*[17] have devised a more rapid approximate method using the absorption at 1 660 cm^{-1} in solid salicylic acid as an internal standard. An ' internal-standard ratio ' (i.s.r.) defined as (C–N stretching absorption area permol of $[CNS]^-$) : (1 660-cm^{-1} absorption area per mol of salicylic acid) is measured for a mull or disc prepared from a mixture of the thiocyanato-compound and salicylic acid. The i.s.r.s. measured for thiocyanato-*S* compounds fall in the range 0—0.6 : 1 whereas for the thiocyanato-*N* compounds the values are all >1.5 : 1. Hassel and Burmeister [12] have used a variation of the method to identify the isomers of $[Pd(PPh_3)_2(CNS)_2]$ and $[Pd(AsPh_3)_2(CNS)_2]$ but the published data otherwise refer to simple metal thiocyanates rather than to mixed-ligand complexes. To establish the general validity of the method we have measured i.s.r.s for a number of reference complexes of known structure as well as for our own new complexes.

The results in Table 2 (values for reference complexes are italicised) [2,7,12,18] show that the i.s.r. values fall quite clearly into two groups: 0.3—0.6 : 1 for M–SCN complexes

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TABLE 2

C–N Stretching bands (cm^{-1}) and absorption intensities relative to salicylic acid (1 660 cm^{-1}) internal standard (Nujol mulls)

Complex	ν(C–N)	$\nu_{\frac{1}{2}}$	Internal standard ratio (i.s.r.)	Ref.
$[Pd(PPh_3)_2(NCS)_2]$	*2 095*	*40*	*1.6*	2, 12, 18
$[Pt(PPh_3)_2(NCS)_2]$	*2 099*	*38*	*1.7*	2
$[Pd(AsPh_3)_2(NCS)_2]$	*2 084*	*40*	*2.6*	2, 12, 18
$[Pt(AsPh_3)_2(NCS)_2]$	*2 104*	*28*	*2.4*	2
$[Pd\{CH_2(PPh_2)_2\}(SCN)_2]$	*2 100*	*12*	*0.51*	7, 8
$[Pt\{CH_2(PPh_2)_2\}(SCN)_2]$	2 115 [2 124 (sh)]	15	0.55	
$[Pd\{CH_2(PPh_2S)_2\}(SCN)_2]$	2 110	13	0.60	
$[Pt\{CH_2(PPh_2S)_2\}(SCN)_2]$	2 111 2 119	9 9 }	0.61	
$[Pd\{CH_2(PPh_2Se)_2\}(SCN)_2]$	2 103	17	0.34	
$[Pt\{CH_2(PPh_2Se)_2\}(SCN)_2]$	2 107	16	0.47	
$[Pd\{CH_2(AsPh_2)_2\}(SCN)_2]$	2 104 2 116	16 18 }	0.40	
$[Pt\{CH_2(AsPh_2S)_2\}(SCN)_2]$	2 107 2 120	13 11 }	0.53	
$[Pd(Ph_2PC_2H_4PPh_2)(NCS)(SCN)]$	*2 095* *2 122*	*35* *12*	*1.90* *0.49* } *1.2*	7, 8
$[Pd(Ph_2PC_2H_4PPh_2)(NCS)_2]$?	2 077	42	*ca.* 2.3	
$[Pd(Ph_2PC_2H_4PPh_2)_2][Pd(SCN)_4]$	*2 101* *2 106* *2 114*	*11* *8* *5* }	*0.60*	7
$[Pt(Ph_2PC_2H_4PPh_2)_2][Pt(SCN)_4]$	2 101 2 110 2 114 (sh) 2 124	7 9 6 6 }	0.61	
$[Pd(Ph_2PC_2H_4PPh_2)_2][CNS]_2$	2 052	13	0.8	
$[Pt(Ph_2PC_2H_4PPh_2)_2][CNS]_2$	2 050	14	0.85	
$[Pd\{CH_2(AsPh_2)_2\}_2(SCN)_2]$	2 112	7	0.34	
$[Pt\{CH_2(AsPh_2)_2\}(NCS)(SCN)]$	2 098 2 120	35 16	1.51 0.51 } 1.01	
$[Pd(bipy)(NCS)_2]$	*2 100*	*35*	*2.7*	2, 18
$[Pt(bipy)(NCS)_2]$	*2 108*	*45*	*2.7*	2
$[Pd\{(C_5H_4N)_2NH\}(SCN)_2]$	2 110 2 124	13 12	0.50	
$[Pt\{(C_5H_4N)_2NH\}(SCN)_2]$	2 116 2 130	16? 10? } 24	0.51	
$[Pd\{(C_5H_4N)_2CO\}(SCN)_2]$	2 106	18	0.41	

and 1.5—3.0 : 1 for M–NCS complexes. The one or two apparent exceptions are discussed in the following section. Thus, even allowing for the errors inevitably involved in estimating the areas enclosed by the often highly irregular C–N stretching absorption envelopes, the internal-standard method clearly distinguishes between the two thiocyanate orientations. In most cases, even for these solid complexes, a simple measurement of $\nu_{\frac{1}{2}}$ is sufficient to indicate the mode of thiocyanate co-ordination.

DISCUSSION

With the exception of 1,2-bis(diphenylphosphino)-ethane, bis(diphenylarsino)methane, and 2,2′-bipyridyl, all the ligands yielded thiocyanato-*S* complexes in both the palladium and platinum series. The C–N stretching band profiles and the absorptions arising from internal-ligand vibrations in most cases are virtually identical for corresponding palladium and platinum complexes. The two complexes involving $CH_2(PPh_2S)_2$, however, have appreciably different C–N stretching spectra. The C–N stretching absorption appears as a singlet in $[Pt\{CH_2(PPh_2S)_2\}(SCN)_2]$ but as a distinct doublet in $[Pd\{CH_2(PPh_2S)_2\}(SCN)_2]$ (Table 2). Both complexes contain *S*-bonded thiocyanate but the disparity in the spectra suggests that there may be other crystallographic or structural differences between them. In general, the C–N stretching frequencies are a few wavenumbers higher for the platinum complexes than for the corresponding palladium complexes. The difference is not great but appears consistently throughout the series.

Complexes with 1,2-*Bis*(*diphenylphosphino*)*ethane*.—Meek *et al.*[7] prepared the orange Magnus salt $[Pd(Ph_2PC_2H_4PPh_2)_2][Pd(SCN)_4]$ from the reaction of 1,2-bis(diphenylphosphino)ethane with $[Pd(SCN)_4]^{2-}$ in ethanol–dichloromethane at 0 °C. Recrystallisation of the salt from hot (100 °C) dimethylformamide (dmf) yielded the neutral yellow ' mixed-thiocyanato '-complex $[Pd(Ph_2PC_2H_4PPh_2)(NCS)(SCN)]$.[8] In our experiments we have obtained at least one and probably two additional products from the preparative reaction.

The i.r. spectrum of the Magnus salt displays three sharp C–N stretching bands between 2 100 and 2 115 cm^{-1} [Figure (*a*)]. {The spectrum is rather more complicated than is usually the case for complexes containing the $[Pd(SCN)_4]^{2-}$ ion; the ' fine structure ' in the C–N stretching absorption is presumably caused by site-symmetry effects.} In the yellow mixed-thiocyanato-complex $[Pd(Ph_2PC_2H_4PPh_2)(NCS)(SCN)]$ a strong broad Pd–NCS C–N stretching band appears at 2 095 cm^{-1}

and a weaker sharp Pd–SCN band at 2 122 cm^{-1} [Figure (*b*)].[7]

Rapid recrystallisation of the Magnus salt from dmf yields a yellow product in which the two bands associated with the mixed-thiocyanato-complex (2 122, 2 095 cm^{-1}) appear superimposed on an additional broad band ($\nu_{\frac{1}{2}}$ *ca.* 40 cm^{-1}) centred at 2 077 cm^{-1} [Figure (*c*)]. Alternatively, if the preparative reaction is carried out in ethanol at 25—30 °C a brown product is obtained which again exhibits a broad band at 2 077 cm^{-1}, but this time in conjunction with the three sharp high-frequency bands associated with the Magnus salt [Figure (*d*)]. (The Magnus salt also undergoes a distinct orange-to-brown colour change before dissolving in warm dmf.) The band observed at 2 077 cm^{-1} is too broad, and at too high a frequency, for ionic thiocyanate: [19] it clearly must be assigned to *N*-bonded thiocyanate but cannot be associated with the Pd–NCS group in the mixed-thiocyanato-complex. We therefore conclude that the hitherto unreported thiocyanato-*N* complex [Pd($Ph_2PC_2H_4PPh_2$)$(NCS)_2$] must be formed at intermediate stages in the preparative reactions.

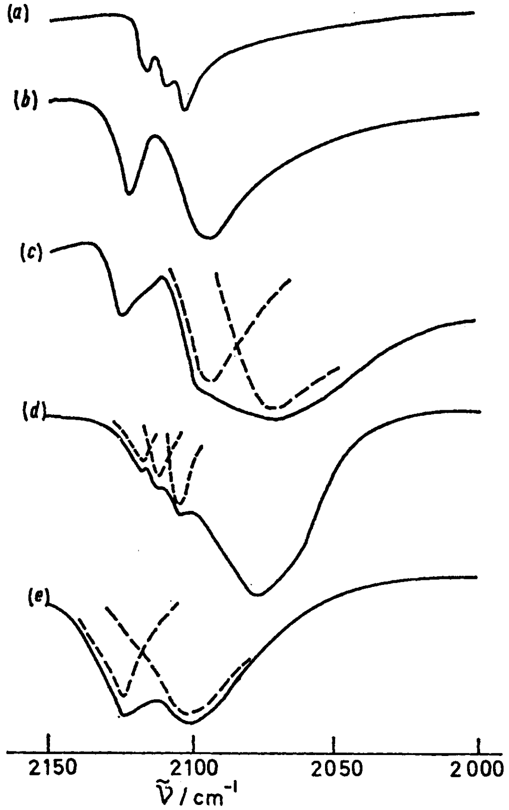

FIGURE C–N Stretching absorptions in (*a*) [Pd($Ph_2PC_2H_4PPh_2$)$_2$][Pd$(SCN)_4$], (*b*) [Pd($Ph_2PC_2H_4PPh_2$)(NCS)(SCN)], (*c*) product from rapid recrystallisation of Magnus salt, (*d*) product from reaction of [Pd$(SCN)_4$]^{2} with $Ph_2PC_2H_4PPh_2$ at 25—30 °C, and (*e*) [Pt{$CH_2(AsPh_2)_2$}(NCS)(SCN)]

At very low temperatures (−78 °C) the white 1 : 2 salt [Pd($Ph_2PC_2H_4PPh_2$)$_2$][CNS]$_2$ separates from the reaction mixture. The relatively sharp C–N stretching band (i.s.r. 0.85 : 1) at 2 052 cm^{-1} is characteristic of the free thiocyanate ion.[14]

The reactions of platinum(II) thiocyanate with 1,2-bis(diphenylphosphino)ethane are very much simpler than those of palladium(II) thiocyanate. At −78 °C we obtain the 1 : 2 salt [Pt($Ph_2PC_2H_4PPh_2$)$_2$][CNS]$_2$ and at higher temperatures the only product is the Magnus salt [Pt($Ph_2PC_2H_4PPh_2$)$_2$][Pt$(SCN)_4$]. These two salts have i.r. spectra and conductivities similar to their palladium analogues. Unlike the palladium complex, however, the platinum Magnus salt dissolves with difficulty in dmf and recrystallises unchanged even after prolonged periods at 100 °C. We have found no evidence for the formation of neutral mixed-thiocyanato- or thiocyanato-*N* complexes in the platinum system. In general, these results reflect the greater lability of palladium(II) compared with platinum(II) complexes and demonstrate a stronger preference on the part of Pt^{II} for the covalent M–SCN as opposed to the more ionic M–NCS linkage.

Complexes with Bis(diphenylarsino)methane.—The reaction of K_2[Pd$(SCN)_4$] with bis(diphenylarsino)methane yields the neutral complex [Pd{$CH_2(AsPh_2)_2$}$_2$$(SCN)_2$] with 1 : 2 metal : ligand stoicheiometry. The single sharp C–N stretching band (i.s.r. 0.34 : 1) at 2 112 cm^{-1} clearly indicates covalent sulphur-bonded thiocyanate.

The ability of bidentate arsine ligands to form palladium(II) or platinum(II) complexes with metal co-ordination numbers greater than four is well established.[9,19-24] The majority of these complexes are five-co-ordinate, especially in solution, but in the solid state co-ordination numbers of six are sometimes achieved. In some cases the interaction with the fifth and sixth ligands is purely electrostatic [23] but in *trans*-octahedral [Pd{*o*-$C_6H_4(AsMe_2)_2$}$_2$$I_2$] the Pd–I bonds appear to have appreciable covalent character.[24]

The i.r. spectrum and stoicheiometry of [Pd{$CH_2(AsPh_2)_2$}$_2$$(SCN)_2$] suggest a six-co-ordinate structure; the very sharp profile of the C–N stretching absorption would be consistent with a *trans*-octahedral arrangement of the sulphur-bonded thiocyanate ligands. However, bis(diphenylarsino)methane is less highly conjugated and less rigid than the diarsines [9,19-24] commonly used to generate five- or six-co-ordinate palladium(II) complexes, and functions in some circumstances as a non-chelate unidentate or bridging ligand.[25,26] Thus, in principle, instead of being monomeric and octahedral the palladium(II) thiocyanate complex may be four-co-ordinate, with unidentate $CH_2(AsPh_2)_2$, or six-co-ordinate and polymeric, with bridging $CH_2(AsPh_2)_2$. If the ligand were to function in a non-chelate manner we would expect reactions of [Pd$(SCN)_4$]$^{2-}$ with less than 2 mol

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equivalents of $CH_2(AsPh_2)_2$ to lead to the formation of complexes with 2 : 3 or 1 : 1 metal : ligand stoicheiometry. In practice, we have obtained the analytically pure 1 : 2 complex as the only product even from solutions containing a large excess of $[Pd(SCN)_4]^{2-}$. The experimental evidence thus points very strongly to a monomeric six-co-ordinate structure for the complex, with chelate $CH_2(AsPh_2)_2$ ligands. The solid structure is not preserved in solution: the C–N stretching absorption in dichloromethane solution shows evidence of *N*-bonded and ionic thiocyanate.

Platinum(II) complexes with co-ordination numbers greater than four are less readily obtained than their palladium(II) analogues,[9,27] and the reaction of $K_2[Pt(SCN)_4]$ with $CH_2(AsPh_2)_2$ yields the neutral 1 : 1 complex $[Pt\{CH_2(AsPh_2)_2\}(CNS)_2]$ as the major product. The C–N stretching absorption appears as a partially resolved doublet with an overall i.s.r. of 1.01 : 1; the absorption envelope may be represented reasonably convincingly as a combination of a sharp Pt–SCN band (i.s.r. 0.51 : 1) at 2 120 cm^{-1} and a broad Pt–NCS band (i.s.r. 1.51 : 1) at 2 098 cm^{-1} [Figure (*e*)]. Accordingly, we formulate the complex as the mixed-thiocyanato-species $[Pt\{CH_2(AsPh_2)_2\}(NCS)(SCN)]$. Reactions of $K_2[Pt(SCN)_4]$ with a large excess of $CH_2(AsPh_2)_2$ lead to the formation of the ionic four-co-ordinate 1 : 2 complex $[Pt\{CH_2(AsPh_2)_2\}_2][CNS]_2$.

Amine Complexes.—At room temperature, palladium(II) and platinum(II) thiocyanates form the thiocyanato-*N* complexes [M(bipy)$(NCS)_2$] with 2,2′-bipyridyl.[2,18] The *S*-bonded palladium isomer is obtained at −78 °C but transforms to the *N*-bonded isomer on warming.[2] Unlike the bipy complexes, the di-2-pyridylamine and di-2-pyridyl ketone complexes contain *S*-bonded thiocyanate and can be heated to the decomposition point without evidence of conversion into the *N*-bonded isomers. The di-2-pyridylamine and di-2-pyridyl ketone molecules are less completely conjugated than bipy and are likely to be less efficient π acceptors; in addition, steric problems will be more severe than with the relatively compact bipy molecule. The electronic and steric effects in the di-2-pyridylamine and di-2-pyridyl ketone complexes will thus favour the formation of thiocyanato-*S* linkages much more strongly than in bipy complexes.

EXPERIMENTAL

Ligands.—Bis[diphenyl(thiophosphoryl)]methane and bis[diphenyl(selenophosphoryl)]methane were prepared from the reactions of $CH_2(PPh_2)_2$ with sulphur in toluene and with K[SeCN] in acetonitrile, respectively, as described by Slinkard and Meek.[28]

Bis[diphenyl(thioarsoryl)]methane. Bis(diphenylarsino)methane $CH_2(AsPh_2)_2$ (4.0 g, 0.0085 mol) was heated under reflux with sulphur (0.8 g, 0.025 mol) in ethanol (100 cm^3) for 12 h. The colourless crystals of $CH_2(AsPh_2S)_2$ which separated on cooling were washed with cold CS_2, recrystallised from ethanol, and dried *in vacuo*, yield 80% (Found: C, 56.6; H, 4.2; S, 11.8. Calc. for $C_{25}H_{22}As_2S_2$: C, 56.0; H, 4.1; S, 11.9%).

The remaining ligands were obtained commercially and recrystallised before use.

Complexes.—Complexes of palladium(II) or platinum(II) thiocyanates were obtained from the reactions of ethanolic solutions of $K_2[Pd(SCN)_4]$ or $K_2[Pt(SCN)_4]$ with equimolar quantities of the ligands in dichloromethane.[7] The precipitated products were collected after 24 h and recrystallised where possible from ethanol–dichloromethane.

1,2-Bis(diphenylphosphino)ethane complexes. The neutral mixed-thiocyanato-complex $[Pd(Ph_2PC_2H_4PPh_2)(NCS)(SCN)]$ and the Magnus salt $[Pd(Ph_2PC_2H_4PPh_2)_2][Pd(SCN)_4]$ ($\Lambda > 35$ S cm^2 mol^{-1}, in $PhNO_2$, $<10^{-4}$ mol dm^{-3}, at 20 °C) were obtained as described by Meek *et al.*[7] Other products of empirical composition $[Pd(Ph_2PC_2H_4PPh_2)(CNS)_2]$ were obtained: (*a*) from the reaction of $Ph_2PC_2H_4PPh_2$ with $K_2[Pd(SCN)_4]$ in ethanol at 25 °C (brown product); (*b*) by dissolving the Magnus salt in dimethylformamide at *ca.* 60 °C and reprecipitating by rapid cooling and addition of diethyl ether (yellow product).

The platinum Magnus salt was obtained in the same way as the palladium analogue and the colourless ionic complexes $[M(Ph_2PC_2H_4PPh_2)_2][CNS]_2$ (M = Pt or Pd) separated on mixing acetone or ethanol solutions of $[M(SCN)_4]^{2-}$ and $Ph_2PC_2H_4PPh_2$ at −78 °C.

Bis(diphenylarsino)methane complexes. Reactions of $K_2[Pd(SCN)_4]$ in metal : ligand proportions varying from 1 : 2 to 4 : 1 yielded $[Pd\{CH_2(AsPh_2)_2\}_2(SCN)_2]$ as the only product. With $K_2[Pt(SCN)_4]$ the neutral 1 : 1 complex $[Pt\{CH_2(AsPh_2)_2\}(NCS)(SCN)]$ obtained as the major product tended to be contaminated with the ionic 1 : 2 complex $[Pt\{CH_2(AsPh_2)_2\}_2][CNS]_2$, particularly in the presence of excess of ligand; precipitation of the ionic complex could be prevented by addition of *ca.* 25% water to the reaction mixture.

Amine complexes. Reactions of the metal thiocyanates with 2 mol equivalents of $(C_5H_4N)_2NH$ or $(C_5H_4N)_2CO$ (L–L) led to the formation of ionic complexes $[M(L–L)_2][CNS]_2$ [ν(C–N) at 2 045 cm^{-1}]. No identifiable products were obtained from the $[Pt(SCN)_4]^{2-}$–$(C_5H_4N)_2CO$ reaction.

Complexes of other ligands. The compounds $Me_2(S)PP(S)Me_2$ and $Et_2(S)PP(S)Et_2$ decomposed on addition to alcoholic solutions of $K_2[Pd(SCN)_4]$ or $K_2[Pd(SCN)_4]$.

Measurement of Internal Standard Ratios.—The method described by Bailey *et al.*[17] was followed. Weighed quantities of the sample and crystalline salicylic acid were intimately mixed and the i.r. spectrum measured as a Nujol mull. The areas under the thiocyanate C–N stretching band and the salicylic acid band at 1 660 cm^{-1} were estimated as the product of the half-peak width ($\nu_{\frac{1}{2}}$) and the maximum absorption intensity. Where the C–N stretching band had more than one component these were resolved as far as possible and estimated separately. Estimated areas based on ' counting squares ' gave substantially the same results as those obtained by the above procedure. Repeated measurements for individual complexes were reproducible within ±15% for M–SCN complexes and probably rather less for M–NCS complexes.

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