Inorganica Chimica Acta, *130* (1987) 43–47

Coordination Chemistry of Higher Oxidation States. Part 24.* Palladium(IV) and Nickel(III) Complexes of Hybrid Thio- and Seleno-ether Ligands

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(Received November 4, 1986)

Abstract

The isolation of the first nickel(III) complexes containing thio- or seleno-ether donor groups is reported, specifically [Ni{o-$C_6H_4(PPh_2)$(EMe)}Br_3] (E = S, Se), [Ni{o-$C_6H_4(PMe_2)$(SeMe)}$_2Br_2$]BF_4, and [Ni{o-$C_6H_4(AsMe_2)$(SeMe)}$_2Br_2$]BF_4. Palladium(IV) and platinum(IV) complexes of o-$C_6H_4(AsMe_2)$(EMe) of type [Pd(L–L)X_4] or [Pt(L–L)X_4] (X = Cl or Br) are also described. The complexes have been characterised by analysis, IR, UV–Vis, multinuclear NMR and ESR spectroscopy as appropriate. The hybrid group VB–VIB donor ligands are in all cases much less effective at stabilising high oxidation state metal centres than diphosphines or diarsines.

Introduction

The ability of diphosphine and diarsine ligands to stabilise high oxidation states of the later transition metals is well known, and our own recent studies have included detailed examination of such complexes of palladium(IV) [2], nickel(III) [3] and nickel(IV) [4]. Neutral group VIB analogues (dithio- or diseleno-ethers) are only moderate σ donors, and whilst platinum(IV) or iridium(IV) complexes are easily obtained [5, 6], attempts to isolate palladium(IV), nickel(III) or nickel(IV) analogues have been unsuccessful.† One possible way of stabilising Pd(IV)–SR_2 or Ni(III)–SR_2 linkages is to use hybrid ligands such as o-C_6H_4(Y)(SMe) (Y = PR_2, AsR_2 etc.) where the strong binding of the Y-group and the rigid o-C_6H_4 backbone [4] will 'encourage' the binding of the group VIB donor group, and this approach is described below.

Results

Six hybrid ligands were used *viz*: o-$C_6H_4(PPh_2)$(EMe), o-$C_6H_4(PMe_2)$(EMe) and o-$C_6H_4(AsMe_2)$(EMe), (E = S, Se).

Palladium

The [Pd(L–L)X_2] (X = Cl or Br, L–L = o-$C_6H_4(PPh_2)$(EMe), o-$C_6H_4(AsMe_2)$(EMe)) were readily obtained from [Pd(MeCN)$_2X_2$] and L–L in CH_2Cl_2, but the o-$C_6H_4(PMe_2)$(EMe) had a strong tendency to form Pd(L–L)$_2X_2$ complexes, which exhibit complex equilibria in solution with the metal bonded to two phosphorus atoms with the EMe and X^- groups competing for the other two coordination positions (*cf.* ref. 8). We were unable to obtain pure 1:1 complexes with these ligands, and since the 1:2 do not oxidise cleanly they were not studied further. Spectroscopic data on the [Pd(L–L)X_2] are given in Table I, along with data on a few platinum(II) analogues for comparison. The data is much as expected when compared with dithioether [9] and diselenoether [10] analogues. The greater complexity of the ^{1}H NMR spectra of [Pt{o-$C_6H_4(AsMe_2)$(SeMe)}X_2] indicates that pyramidal inversion at the Se donor is slow and hence two As–Me resonances are observed (Me′ and Me″, Fig. 1), whereas for [Pd(L–L)X_2] or [Pt{o-$C_6H_4(AsMe_2)$(SMe)}Cl_2] only a single As–Me resonance is observed, since fast inversion makes Me′ and Me″ appear equivalent.

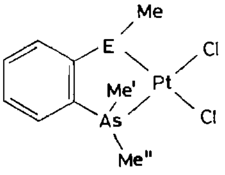

Fig. 1. Structure of [Pt{o-$C_6H_4(AsMe_2)$(EMe)}Cl_2].

The [Pd(L–L)X_2], L–L = o-$C_6H_4(PPh_2)$(SMe), o-$C_6H_4(PPh_2)$(SeMe), were not oxidised by the appropriate halogen, similar behaviour to that observed [2] with Pd(II) bromocomplexes of aryl diphosphines,

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*Part 23 is ref. 1.

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†The sole exceptions are the unstable halopalladate(IV) anions [PdLX_5]$^-$ (L = Me_2S; Me_2Se) [6, 7].

0020-1693/87/$3.50

TABLE I. Selected Spectroscopic Data for M(II) Complexes

Complex	^{1}H (MeMe) (ppm)[a]	^{77}Se{^{1}H} (ppm)[b]	^{195}Pt{^{1}H} (ppm)[c]
$[Pd\{o\text{-}C_6H_4(PPh_2)(SeMe)\}Cl_2]$		431.8(24)[d]	
$[Pd\{o\text{-}C_6H_4(PPh_2)(SeMe)\}Br_2]$		431.5(25)[e]	
$[Pt\{o\text{-}C_6H_4(AsMe_2)(SMe)\}Cl_2]$	1.90(10), 3.0(23)		−4200
$[Pt\{o\text{-}C_6H_4(AsMe_2)(SeMe)\}Cl_2]$	1.85(23), 1.90(23) 2.80(40)	410.1(533)[f]	−4268
$[Pt\{o\text{-}C_6H_4(AsMe_2)(SeMe)\}Br_2]$	1.95(21), 1.98(21) 2.88(40)	347.6(308)[f]	−4702
$[Pd\{o\text{-}C_6H_4(AsMe_2)(SeMe)\}Cl_2]$	1.85, 2.75	482.6	
$[Pd\{o\text{-}C_6H_4(AsMe_2)(SeMe)\}Br_2]$	1.92, 2.85	421.8	
$[Pd\{o\text{-}C_6H_4(NMe_2)(SeMe)\}Cl_2]$	2.4, 2.95	361.0	

[a] In $CDCl_3$ or CD_2Cl_2 relative to internal TMS, $^3J(^1H-^{195}Pt)$ in parenthesis. [b] In CH_2Cl_2 relative to external neat Me_2Se. [c] In dmso relative to external Na_2PtCl_6 in H_2O. [d] $^2J(^{31}P-^{77}Se)$ in parenthesis: $^{31}P\{^1H\} = 57.1$ ppm. [e] $^2J(^{31}P-^{77}Se)$ in parenthesis: $^{31}P\{^1H\} = 60.5$ ppm. [f] $^1J(^{77}Se-^{195}Pt)$ in parenthesis.

suggesting that the donor strength of the ligands needs to be increased. In keeping with this the complexes of $o\text{-}C_6H_4(AsMe_2)(SMe)$ and $o\text{-}C_6H_4(AsMe_2)(SeMe)$ were readily oxidised by cautious treatment with X_2 to orange $[Pd(L-L)X_4]$. The Pd(IV) formulation follows from comparison of the UV–Vis and IR spectra (Table II) with those of $[Pd(diphosphine)X_4]$ [2], but the complexes are too unstable in solution for NMR studies. Platinum(IV) analogues $[Pt(L-L)X_4]$ are readily obtained, and for these the ^{77}Se and ^{195}Pt NMR spectra are clear evidence of the presence of Pt(IV). For example oxidation of $[Pt\{o\text{-}C_6H_4(AsMe_2)(SeMe)\}Cl_2]$ results in substantial high frequency shifts in both $\delta(^{77}Se)$ and $\delta(^{195}Pt)$ *ca.* 136 and *ca.* 1630 ppm respectively (*cf.* refs. 6 and 11). Although Pd(IV) complexes of diamines are known [2, 12], chlorine in CH_2Cl_2 decomposed $[Pd\{o\text{-}C_6H_4(NMe_2)(SeMe)\}Cl_2]$ to a brown material of low carbon content.

Nickel

The ligands $o\text{-}C_6H_4(PMe_2)(SMe)$ [4], $o\text{-}C_6H_4(AsMe_2)(SMe)$ [13], $o\text{-}C_6H_4(PMe_2)(SeMe)$, and $o\text{-}C_6H_4(AsMe_2)(SeMe)$ form $[Ni(L-L)_2X_2]$ which range in colour from yellow–green to blue–green, and have diffuse reflectance spectra and magnetic moments typical of tetragonal nickel(II) complexes. They dissolve in CH_2Cl_2 or MeCN to give rather unstable (especially X = Cl) red or brown solutions which have electronic spectra consistent with the formation of $[Ni(L-L)_2X]^+$. The phenylphosphine analogues $o\text{-}C_6H_4(PPh_2)(SMe)$ and $o\text{-}C_6H_4(PPh_2)(SeMe)$ also give green $[Ni(L-L)_2X_2]$ which in chlorocarbon solvents dissociate into purple planar $[Ni(L-L)X_2]$ and free ligand [14, 15]. Red–brown $[Ni(L-L)_2X]ClO_4$ are also known [14].

Cautious bromination of $[Ni(L-L)Br_2]$ ($L-L = o\text{-}C_6H_4(PPh_2)(SMe), o\text{-}C_6H_4(PPh_2)(SeMe)$) gave black $[Ni(L-L)Br_3]$, which have electronic spectra consistent with a five coordinate square pyramidal geometry as was established for $[Ni(Ph_2PCH_2CH_2PPh_2)Br_3]$ [3]. ESR spectroscopy in freshly prepared CH_2Cl_2 containing a little bromine to suppress decomposition revealed each to have a four-line resonance ($g_{av} = 2.12$, $A_{iso} = 35$ G (S), $g_{av} = 2.15$, $A_{iso} = 43$ G (Se)) due to coupling with the apical bromine ($I = \frac{3}{2}\,^{79,81}Br$) (*cf.* ref. 3). The powders give isotropic spectra. ESR spectra suggest that $[Ni\{o\text{-}C_6H_4(PPh_2)(SMe)\}_2Br_2]$ and $[Ni\{o\text{-}C_6H_4(PPh_2)(SMe)\}_2Br]^+$ also give $[Ni\{o\text{-}C_6H_4(PPh_2)(SMe)\}Br_3]$ upon treatment with Br_2, but the latter could not be separated from the oxidised ligand also present. The Ni(III) complexes are markedly less stable than the diphosphine analogues [3]; both decompose in hours at room temperature, and in ~2 days at *ca.* −20 °C. Attempts to isolate the corresponding Ni(III) chlorides were unsuccessful, although treatment of $[Ni(L-L)Cl_2]$ with Cl_2/CH_2Cl_2 and immediately freezing to −196 °C gave glasses which exhibited isotropic ESR spectra $g \sim 2.12$ (S), 2.17 (Se), consistent with transient generation of the nickel(III) complexes. Treatment of $[Ni(L-L)Cl_2]$ with nitrosyl chloride, which is a less destructive oxidant than Cl_2 [16], in these cases generated nitrosyl complexes rather than nickel(III).

The nickel(II) complexes of the alkyl substituted ligands $o\text{-}C_6H_4(AsMe_2)(EMe)$ behaved rather differently. In CH_2Cl_2 or MeCN solution treatment with a variety of oxidants including Cl_2, NOCl, $NOBF_4$ and Br_2 caused the initially red or brown solutions to turn yellow–green or brown (depending upon L–L and X), which then decolourised in seconds. Treatment of the solid nickel(II) complexes with concentrated HNO_3 gave green colours which faded rapidly. In two cases $[Ni(L-L)_2Br_2]$ ($L-L = o\text{-}C_6H_4(PMe_2)(SeMe)$, $o\text{-}C_6H_4(AsMe_2)(SeMe)$) cautious treatment in the cold (0 °C) with conc. HNO_3, followed by addition to 40% aqueous HBF_4 gave $[Ni(L-L)_2Br_2]BF_4$ as unstable yellow–green or deep green solids respectively (Table III). The spectroscopic properties of these materials are similar to those of well known Ni(III)

TABLE II. Physical Data on Pd(IV) and Pt(IV) Complexes

Complex	Colour	C (%)[a]	H (%)	ν(M–X) (cm^{-1})	$10^{-3} E_{max}$ (cm^{-1})[b]	^{77}Se{^{1}H} (ppm)[d]	^{195}Pt{^{1}H}(ppm)[d]
$[Pd\{o\text{-}C_6H_4(AsMe_2)(SMe)\}Cl_4]$	orange	23.0(22.8)	2.8(2.7)	345(sh), 336, 329, 320(sh)	20.1(sh), 22.9, 28.6		
$[Pd\{o\text{-}C_6H_4(AsMe_2)(SMe)\}Br_4]$	orange	16.4(16.5)	2.1(2.0)	~250(vbr)	21.9, 28.5		
$[Pt\{o\text{-}C_6H_4(AsMe_2)(SMe)\}Cl_4]$	yellow	19.1(19.1)	2.0(2.1)	343(sh), 336, 324, 299(sh)	28.1(sh), 33.8(2490)[c]		−2346
$[Pd\{o\text{-}C_6H_4(AsMe_2)(SeMe)\}Cl_4]$	orange	20.9(20.6)	2.4(2.5)	336(sh), 327, 305	22.0, 28.7		
$[Pd\{o\text{-}C_6H_4(AsMe_2)(SeMe)\}Br_4]$	orange	14.5(15.4)	1.6(1.9)	242(sh), 230, 214	24.5, 29.7		
$[Pt\{o\text{-}C_6H_4(AsMe_2)(SeMe)\}Cl_4]$ [f]	yellow	17.4(17.6)	2.0(2.1)	344, 332, 317, 300	22.7(230), 27.2(730)[e] 33.0(1200)	546	−2636
$[Pt\{o\text{-}C_6H_4(AsMe_2)(SeMe)\}Br_4]$	orange	14.0(13.7)	1.7(1.6)	220(vbr)	25.5(510), 31.4(1700)[e]		

[a] Calculated value in parenthesis. [b] Diffuse reflectance unless indicated. [c] In dmso. ϵ (dm^3 cm^{-1} mol^{-1}) in parenthesis. [d] See footnote to Table I. [e] In MeCN. [f] ^{1}H NMR: 2.05(12), 2.10(12), 2.70(70).

diphosphine and diarsine complexes [3, 17, 18], which have (D_{2h}) ***trans*** pseudooctahedral geometry. Particularly characteristic are the electronic spectra (Table III) which have a very weak absorption at *ca.* 13 000 cm^{-1} and intense bands at >23 000 cm^{-1}. The ESR spectra are also generally consistent with this geometry [3, 19] but we have been unable to observe the extensive hyperfine structure expected, possibly due to the low symmetry. The observed g values are $[Ni\{o\text{-}C_6H_4(PMe_2)(SeMe)\}_2Br_2]^+$ 1.99 and $[Ni\{o\text{-}C_6H_4(AsMe_2)(SeMe)\}_2Br_2]^+$ 2.03.

Bromine oxidation of $[Ni\{o\text{-}C_6H_4(PMe_2)(SeMe)\}_2Br_2]$ in CH_2Cl_2 gave an unstable solution which exhibited an ESR spectrum (−196 °C CH_2Cl_2 glass g_{av} 2.04) very similar to those of $[Ni\{o\text{-}C_6H_4(PPh_2)(EMe)\}Br_3]$, *i.e.* a four line pattern with further ill-defined coupling superimposed, suggesting one ligand has been removed to give $[Ni\{o\text{-}C_6H_4(PMe_2)(SeMe)\}Br_3]$. Similar halogen oxidation of $[Ni\{o\text{-}C_6H_4(AsMe_2)(EMe)\}_2Br_2]$, $[Ni\{o\text{-}C_6H_4(PMe_2)(SMe)\}_2Br_2]$ and of the corresponding chlorocomplexes followed by immediate quenching to −196 °C, gave glasses which exhibited broad generally structureless ESR spectra with $g = 2.0–2.1$ which disappeared in seconds on thawing. These spectra and the accompanying colour changes suggest that transient 1:1 nickel(III) complexes are formed by all these ligands, but their instability and the lack of resolvable structure on the ESR resonances preclude a more definite characterisation.

Discussion

The successful isolation of palladium(IV) complexes of the $o\text{-}C_6H_4(AsMe_2)(EMe)$ (E = S, Se) but not with the $o\text{-}C_6H_4(PPh_2)(EMe)$ demonstrates that (*cis*)$[Pd(L–L)X_4]$ complexes can be obtained with thio- or selenoether donors supported by a very strong σ-donor group like $AsMe_2$. Stabilisation of $t_{2g}{}^6$Pd(IV) requires a strong ligand field [2] which will maximise the LFSE.

For nickel(III) only four bromocomplexes were obtained, two of type $[Ni(L–L)Br_3]$ and two $[Ni(L–L)_2Br_2]BF_4$. The greater instability of chloro–nickel(III) complexes of weaker donor ligands has been observed previously [3, 16] and is ascribed to the poorer binding of the neutral ligand to the harder $Ni^{III}–Cl_x$ acceptor grouping compared with $Ni^{III}–Br_x$. It would appear from these studies that the hybrid selenoethers bind to nickel(III) better than the thioether analogues since the $[Ni(L–L)_2Br_2]^+$ were only isolated with the former. We have suggested [6] that the larger less electronegative selenoethers are better donors towards platinum metals, but it is less clear why the same behaviour should be exhibited towards a smaller hard first row metal.

There is currently considerable interest in nickel(III) sites in hydrogenases [19, 20] some at least of

TABLE III. Selected Data on the Nickel Complexes

Complex	Colour	E_{max} (10^3 cm^{-1}) (ϵ_{mol} (cm^{-1} mol^{-1} dm^3))[a]	ν(Ni–X) (cm^{-1})[b]	C (%)[c]	H (%)
$[Ni\{o\text{-}C_6H_4(PMe_2)(SeMe)\}_2Cl_2]$	green	20.4(–)sh, 28.0(–)(sh), (CH_2Cl_2)	230	36.5(36.4)	4.4(4.3)
$[Ni\{o\text{-}C_6H_4(PMe_2)(SeMe)\}_2Br_2]$	yellow–brown	20.2(–)sh, 26.45(–), (CH_2Cl_2)	no	31.3(31.6)	3.9(3.8)
$[Ni\{o\text{-}C_6H_4(AsMe_2)(SeMe)\}_2Cl_2]$	green	18.9(–), 29.4(–)sh, (CH_2Cl_2)	243	32.4(32.1)	3.6(3.8)
$[Ni\{o\text{-}C_6H_4(AsMe_2)(SeMe)\}_2Br_2]$	yellow–green	18.2(–), 28.8(–), (CH_2Cl_2)	no	28.0(28.1)	3.5(3.4)
$[Ni\{o\text{-}C_6H_4(PMe_2)(SeMe)\}_2Br_2]BF_4$	yellow–green	13.7(30), 24.4(1450), (MeCN)	no	27.8(28.1)	3.5(3.4)
$[Ni\{o\text{-}C_6H_4(AsMe_2)(SeMe)\}_2Br_2]BF_4$	bright green	12.9(40), 23.9(3870), 28.8(4340)sh, (MeCN)	184	25.5(25.2)	3.1(3.0)
$[Ni\{o\text{-}C_6H_4(PPh_2)(SMe)\}Br_3]$	black	12.1, 18.2, 29.3(dr)	307, 232	38.0(37.6)	2.9(2.8)
$[Ni\{o\text{-}C_6H_4(PPh_2)(SeMe)\}Br_3]$	brown–black	*ca.* 13.1, 18.1, 24.2(sh), 28.9(dr)	no	34.6(34.8)	2.5(2.6)

[a] In solvent specified, the Ni(II) complexes are unstable in solution and ϵ_{mol} was not accurately determined, dr = diffuse reflectance diluted with $BaSO_4$. [b] Nujol mull, no = not observed. [c] Calculated value in parenthesis.

which have sulphur donor environments [21]. It is not yet clear whether sulphido (S^{2-}), thiolo (RS^-) or thioether (RSR) donors or some combination of these are involved. The complexes reported in this present study appear to be the first isolated examples of thio- or selenoether coordination to nickel(III)*. In comparison with the diphosphine ($o\text{-}C_6H_4(PMe_2)_2$) or diarsine ($o\text{-}C_6H_4(AsMe_2)_2$) analogues which give very stable nickel(III) complexes and the only currently known nickel(IV) complexes with any neutral ligand [4], the replacement of one group VB donor group by –SMe or –SeMe to form $o\text{-}C_6H_4(PMe_2)(EMe)$ or $o\text{-}C_6H_4(AsMe_2)(EMe)$ has a very adverse effect upon the ligands ability to support high oxidation state metal centres.

Experimental

Physical measurements were made as described in previous parts of this series.

The ligands $o\text{-}C_6H_4(PPh_2)(SMe)$ [23], $o\text{-}C_6H_4(PPh_2)(SeMe)$ [23], $o\text{-}C_6H_4(PMe_2)(SMe)$ [24], $o\text{-}C_6H_4(PMe_2)(SeMe)$ [25], $o\text{-}C_6H_4(AsMe_2)(SeMe)$ [25] were made by literature methods. $o\text{-}C_6H_4(AsMe_2)(SMe)$ was obtained from $o\text{-}C_6H_4Br(SMe)$ and $NaAsMe_2$ in tetrahydrofuran. Boiling point 76–80 °C/0.1 torr 33%. $[Pd\{o\text{-}C_6H_4(PPh_2)(SMe)\}X_2]$ [26], $[Ni\{o\text{-}C_6H_4(PPh_2)(SMe)\}X_2]$ [14], $[Ni\{o\text{-}C_6H_4(PPh_2)(SMe)\}_2X_2]$ [14], $[Ni\{o\text{-}C_6H_4(PMe_2)(SMe)\}_2X_2]$ [4], $[Ni\{o\text{-}C_6H_4(AsMe_2)(SMe)\}_2X_2]$ [13] and $[Pd\{o\text{-}C_6H_4(AsMe_2)(SMe)\}X_2]$ [13] were made by literature methods, and $[Pd\{o\text{-}C_6H_4(PPh_2)(SeMe)\}X_2]$ from $o\text{-}C_6H_4(PPh_2)(SeMe)$ and $[Pd(MeCN)_2X_2]$ in CH_2Cl_2. All had satisfactory analyses.

Dichloro(o-dimethylarsinophenylmethylselenide) palladium(II) [Pd{o-C$_6$H$_4$(AsMe$_2$)(SeMe)}Cl$_2$]

$[PdCl_2(MeCN)_2]$ (0.26 g, 1 mmol) was dissolved in dichloromethane (30 cm^3) in a 100 ml round bottom 3-neck flask fitted with a 'suba seal' septum cap and nitrogen inlet. The ligand (0.275 g, 1 mmol) was dissolved in dichloromethane (20 cm^3) and added slowly dropwise to the rapidly stirred solution of the palladium salt over a period of 30 min. The solution was stirred for a further 3 h, when a deep yellow precipitate was filtered, washed with diethylether, and dried *in vacuo*. Yield 0.33 g, 74%. *Anal.* Found: C, 24.1; H, 3.0. Calc. for $C_9H_{13}AsCl_2PdSe$: C, 23.9; H, 2.9%. The other Pd(II) and Pt(II) complexes of this ligand were made similarly.

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*After completion of our study a preliminary account of the formation in solution of Ni(III) complexes of modified triazene-1-oxides containing a thioether function appeared, but the complexes have not been isolated (see ref. 22).

[Pd{*o*-$C_6H_4(AsMe_2)(SeMe)$}Br_2]. *Anal.* Found: C, 19.8; H, 2.4. Calc. for $C_9H_{13}AsBr_2PdSe$: C, 20.8; H, 2.4%.

[Pt{*o*-$C_6H_4(AsMe_2)(SeMe)$}Cl_2]. *Anal.* Found: C, 20.0; H, 2.5. Calc. for $C_9H_{13}AsCl_2PtSe$: C, 20.0; H, 2.4%.

[Pt{*o*-$C_6H_4(AsMe_2)(SeMe)$}Br_2]. *Anal.* Found: C, 17.2; H, 2.1. Calc. for $C_9H_{13}AsBr_2PtSe$: C, 17.1; H, 2.1%.

[Pd{*o*-$C_6H_4(NMe_2)(SeMe)$}Cl_2] was also made similarly. *Anal.* Found: C, 27.8; H, 3.4. Calc. for $C_9H_{13}Cl_2NPdSe$: C, 27.6; H, 3.3%.

Tetrachloro(o-dimethylarsinophenylmethylselenide)palladium(IV)

Finely powdered [Pd(L–L)Cl_2] was suspended in dry carbon tetrachloride, and a very small excess of Cl_2–CCl_4 was added slowly with rapid stirring. After 5 min, the dark orange solid was filtered, washed with dry carbon tetrachloride but not pumped dry (care should be taken not to pump damp air through the product), and then dried *in vacuo*. Yield 73%.

The other complexes of this ligand and of *o*-$C_6H_4(AsMe_2)(SMe)$ were prepared in a similar manner.

Dichlorobis(o-dimethylphosphinophenylmethylselenide)nickel(II) [Ni{o-$C_6H_4(PMe_2)(SeMe)$}$_2Cl_2$]

[$NiCl_2 \cdot 6H_2O$] (0.20 g; 0.48 mmol) was dissolved in ethanol (20 cm^3) and the system was purged with nitrogen. The solution was warmed to *ca.* 40 °C and the ligand (0.38 mmol; 1.65 mmols) was added slowly to the rapidly stirred solution of the nickel salt. The solution was stirred for a further 20 min. The solvent was reduced to *ca.* 5 cm^3. To this was added copious quantities of Et_2O. This gave a yellow–brown precipitate which was isolated by filtration, washed with Et_2O (3 × 15 cm^3) and dried *in vacuo*. Yield 0.10 g, 20%.

The other Ni^{II} complexes, of this type, were made similarly.

Dibromobis(o-dimethylarsinophenylmethylselenide)nickel(III) tetrafluoroborate [Ni{o-$C_6H_4(AsMe_2)(SeMe)$}$_2Br_2$]BF_4

[Ni{*o*-$C_6H_4(AsMe_2)(SeMe)$}$_2Br_2$] (as prepared by the above method) was dissolved in conc. HNO_3 (containing 1 drop conc. HBr) (5 cm^3) at 0 °C. This gave a dark green solution which was filtered into conc. HBF_4 (10 cm^3) precooled to 0 °C. After five minutes a green precipitate was formed which was isolated by filtration and carefully washed with ice-cold water (2 × 5 cm^3), Et_2O (3 × 10 cm^3) and dried *in vacuo*.

The complex [Ni{*o*-$C_6H_4(PMe_2)(SeMe)$}$_2Br_2$]BF_4 was similarly prepared.

Acknowledgement

We thank the SERC for support.

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