Anal. Calcd for $KCrOF_4$: Cr, 28.40; F, 41.5. Found: Cr, 28.26; F, 42.5.

Acknowledgment. We wish to acknowledge gratefully the support of the donors of the Petroleum Research Fund, administered by the American Chemical Society.

Registry No. $CrOF_3$, 43997-25-7; CrO_3, 1333-82-0; CrO_2F_2, 7788-96-7; $KCrOF_4$, 68258-60-6; CrF_5, 14884-42-5; ClF, 7790-89-8; KF, 7789-23-3.

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Electron Spin Resonance Spectra of the One-Electron-Reduction Products of Stannic Chloride Adducts of Bis(dithiooxalato)nickelate(II), -palladate(II), and -platinate(II) Complexes

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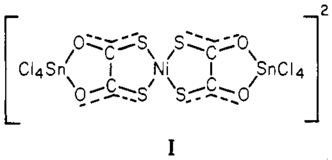
Stannic chloride forms 1:1 and 1:2 adducts with bis(dithiooxalato)nickel(II) and bis(dithiooxalato)palladium(II) anionic complexes, $[M(S_2C_2O_2)_2]^{2-}$, M = Ni, Pd, and a crystal structure determination for the 1:2 adduct of the nickel complex (I) showed that the $SnCl_4$ molecules are coordinated to the α-diketone oxygen atoms of the dithiooxalate ligands, which are themselves S-bonded to nickel as in the parent bis(dithiooxalato) complex. The coordination about Ni is square planar and that about Sn is octahedral.[1,2]



I

Unlike the parent bis(dithiooxalato)metalate complexes, the $SnCl_4$ adducts undergo well-defined reversible electrochemical reductions. The 1:1 adducts undergo a single reversible one-electron reduction while the 2:1 adducts undergo reversible reduction in two one-electron steps. It has been suggested that these reductions are ligand rather than transition metal based, the added electrons going into a ligand π-antibonding orbital whose energy is lowered relative to that in the parent bis(dithiooxalate) complex by adduct formation with $SnCl_4$.[1,2]

In the course of our work on the spectroelectrochemistry of nickel(II) complexes with sulfur ligands,[3] we have measured the ESR spectra of the one-electron-reduction products of the complexes described above by in situ electrolysis. We have also studied the electrochemical reduction of the 1:1 and 1:2 $SnCl_4$ adducts of the bis(dithiooxalato)platinum(II) dianion, $[Pt(S_2C_2O_2)_2]^{2-}$, and have measured the ESR spectra of the one-electron-reduction products. We have also examined the cyclic voltammetry of the parent $[M(S_2C_2O_2)_2]^{2-}$ complexes for comparison with the previously published results for the $SnCl_4$ adducts.

Experimental Section

Preparation of Compounds. Bis(tetraphenylphosphonium) Bis(dithiooxalato)metalates(II). These were prepared in a manner similar to that described previously by Coucouvanis et al.[1,2] for the corresponding bis(benzyltriphenylphosphonium) salts, with the exception that the products were recrystallized from nitromethane/diethyl ether instead of dimethylformamide/ether. The compounds were obtained as the 1:1 nitromethane solvates (M = Ni, Pd) or as the 2:1 nitromethane solvate (M = Pt). This was verified by ^{1}H NMR and elemental analysis. $[Ph_4P]_2[Ni(S_2C_2O_2)_2]\cdot CH_3NO_2$: mp 285 °C. Anal. Calcd for $C_{53}H_{43}NNiO_6P_2S_4$: C, 61.27; H, 4.17. Found: C, 61.56; H, 4.78. $[Ph_4P]_2[Pd(S_2C_2O_2)_2]\cdot CH_3NO_2$: mp 227 °C. Anal. Calcd for $C_{53}H_{43}NP_6P_2PdS_4$: C, 58.58; H, 3.99. Found: C, 58.35; H, 4.43. $[Ph_4P][Pt(S_2C_2O_2)_2]\cdot 2CH_3NO_2$: mp 219 °C. Anal. Calcd for $C_{54}H_{46}N_2O_8P_2PtS_4$: C, 52.46; H, 3.75. Found: C, 52.50; H, 4.35.

Stannic Chloride Adducts. Attempts were made to prepare these by the method described by Coucouvanis et al. for the corresponding bis(benzyltriphenylphosphonium) salts. A pure product was obtained only in the case of the 1:1 adduct with the bis(dithiooxalato)nickelate(II) complex. $[Ph_4P]_2(Ni(S_2C_2O_2)_2(SnCl_4)]$: mp 204 °C. Anal. Calcd for $C_{52}H_{40}Cl_4NiO_4P_2S_4Sn$: C, 50.44; H, 3.26. Found: C, 50.36; H, 3.61. In all other cases addition of $SnCl_4$ to a CH_2Cl_2 solution of the bis(dithiooxalato)metalate(II) complex in a 1:1 or 2:1 mole ratio produced an immediate color change, indicating that adduct formation had taken place, but attempts to crystallize these adducts by addition of pentane resulted only in oils, which could not be recrystallized from common solvents. The formation of the 1:1 and 1:2 adducts was verified by cyclic voltammetry of solutions of the bis(dithiooxalato)metalate(II) complex and $SnCl_4$ in appropriate mole ratios in $CHCl_2$ and by the ESR spectra of the one-electron-reduction products (see Results and Discussion).

Electrochemistry. Electrochemical measurements were carried out at a platinum electrode by using a PAR 173 potentiostat with a PAR 179 digital coulometer with IR compensation, an ECG 175 universal programmer, and an HP 7046A X-Y recorder. The reference electrode was Ag/AgCl (0.1 M LiCl in CH_2Cl_2) separated from the voltammetric cell by a 0.1 M $[Bu_4N]ClO_4$ in CH_2Cl_2 salt bridge. Measurements were carried out in dichloromethane (0.1 M $[Bu_4N]ClO_4$ supporting electrolyte) or in acetonitrile (0.1 M $[Bu_4N]ClO_4$ supporting electrolyte). All potentials were internally referenced to the potential for the one-electron oxidation of ferrocene (+0.46 V vs. Ag/AgCl) or the one-electron oxidation of $[Pt((CN)_2C_2S_2)_2]^{2-}$ (+0.16 V vs. Ag/AgCl) as described previously.[3]

Electron Spin Resonance Spectra. X-band electron spin resonance spectra were recorded with a Varian E4 spectrometer. The electrochemically produced species were generated in situ on a platinum electrode by controlled-potential electrolysis using a three-electrode configuration,[3] at potentials slightly beyond the measured redox potential of the complex. Electrolyses in this cell could be carried out at ambient or lower temperatures with use of the Varian variable-temperature attachment. Frozen-solution spectra were obtained by freezing the contents of the in situ cell after electrolysis.

The method used to simulate frozen-solution spectra has been described previously.[3]

Results and Discussion

(a) Ni and Pd Complexes. The only $SnCl_4$ adduct of the bis(tetraphenylphosphonium) bis(dithiooxalato)metalate(II) complexes that could be obtained in pure crystalline form is the 1:1 adduct $[Ph_4P]_2[Ni(S_2C_2O_2)_2SnCl_4]$. However, it is clear from the cyclic voltammetry of CH_2Cl_2 solutions containing the parent bis(dithiooxalato)metalate(II) complexes and $SnCl_4$ in the appropriate mole ratios, that the 1:1 and 1:2 adducts are readily formed in solution. The cyclic voltammetric parameters for the adducts are given in Table I. The $E_{1/2}$ values are all about 0.4 V more positive than those reported previously for the corresponding bis(benzyltriphenylphosphonium) salts, but this difference is probably due to the different reference systems used for measuring the potentials (see Experimental Section). The relative $E_{1/2}$ values between different complexes and between different waves in the same complex in the case of the 1:2 adducts agree well with those found previously for the corresponding bis(benzyltriphenylphosphonium) salts.[1,2]

Electrolysis of solutions of the $SnCl_4$ adducts in the in situ cell at room temperature at potentials corresponding to the first one-electron-reduction step produced strong ESR signals. Representative spectra are shown in Figures 1 and 2, and the ESR parameters are listed in Table II.

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Table I. Cyclic Voltammetry Parameters (V) for the Reduction of $[M(S_2C_2O_2)_2]^{2-}$ (M = Ni, Pd, Pt) Complexes and Their 1:1 and 1:2 Adducts with $SnCl_4$ in CH_2Cl_2 Solution

	1st redn			2nd redn		
complex	E_r°	ΔE_{pp}(at 100, 200 mV s^{-1})	i_p^r/i_p^r [c]	E_r°	ΔE_{pp}(at 100, 200 mV s^{-1})	i_p^r/i_p^f [c]
$[Ni(S_2C_2O_2)_2]^{2-}$	−2.03[a]					
$[Ni(S_2C_2O_2)_2(SnCl_4)]^{2-}$	−0.53	0.13, 0.14	1.0			
$[Ni(S_2C_2O_2)_2(SnCl_4)_2]^{2-}$	−0.15	0.11, 0.16	1.0	−0.51	0.12, 0.18	0.9
$[Pd(S_2C_2O_2)_2]^{2-}$	−2.05[a]					
$[Pd(S_2C_2O_2)_2(SnCl_4)]^{2-}$	−0.54	0.09, 0.10	1.0			
$[Pd(S_2C_2O_2)_2(SnCl_4)_2]^{2-}$	−0.23	0.08, 0.10	1.0	−0.52	0.13, 0.14	0.9
$[Pt(S_2C_2O_2)_2]^{2-}$	<−2.05[b]					
$[Pt(S_2C_2O_2)_2(SnCl_4)]^{2-}$	−0.15	0.09, 0.10	1.0			
$[Pt(S_2C_2O_2)_2(SnCl_4)_2]^{2-}$	−0.15	0.08, 0.90	1.0	−0.54	0.11, 0.12	0.9

[a] Irreversible reduction for sweep rates up to 5 V s^{-1}. The peak cathodic potential is given. [b] Reduction process not observed within the solvent window. [c] At 100 mV s^{-1} scan rate.

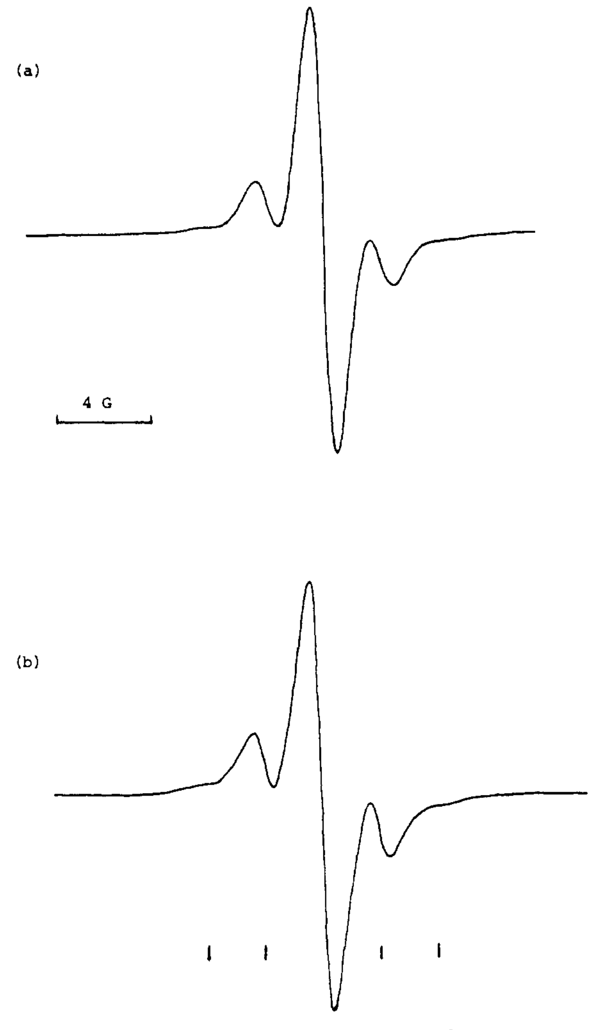

Figure 1. ESR spectra of $[Ni(S_2C_2O_2)_2(SnCl_4)_2]^{3-}$ electrogenerated in CH_2Cl_2 at 17 °C: (a) experimental; (b) simulated (parameters given in Table IIA). The stick spectrum shows the position of satellites due to 7% of two magnetic tin isomers and 13.7% of one magnetic tin isomer.

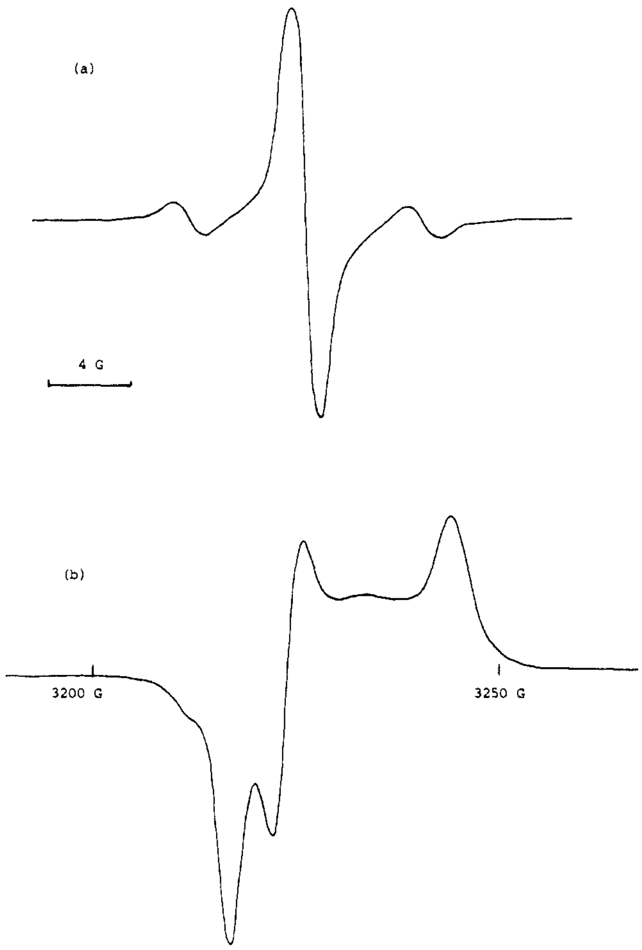

Figure 2. ESR spectra of $[Pd(S_2C_2O_2)_2(SnCl_4)]^{3-}$ electrogenerated in CH_2Cl_2 at 20 °C: (a) solution spectrum at 20 °C; (b) frozen-solution spectrum at −160 °C, 9.055 GHz.

The solution spectra show a strong central line with a *g* value very close to the free-electron value and satellite lines due to hyperfine coupling with the magnetic isotopes of Sn (^{117}Sn, 7.67%, $I = ^1/_2$; ^{119}Sn, 8.68%, $I = ^1/_2$). In the case of the Ni complexes, there are no other magnetic nuclei that could give rise to such satellites, and the intensities of the satellites relative to the central peaks are correctly simulated by using the known natural abundances of the Sn isotopes. In the case of the 1:2 complex, satellites are seen for the 27.35% of species with one magnetic Sn nucleus per molecule, as well as for the 2.67% of species that have two magnetic Sn nuclei present in the same molecule (Figure 1). The lines were too broad to allow resolution of the splittings due to ^{117}Sn and ^{119}Sn. In the case of the Pd complexes, the only nuclear species apart from $^{117,119}Sn$ that could give rise to satellites is ^{105}Pd (22.23%). However, this is an $I = ^5/_2$ nucleus and so cannot give rise to the satellite spectrum observed. Any ^{105}Pd coupling must be less than the line widths, since the ^{105}Pd satellites would have been sufficiently intense to have been observed (approximately half of the intensity of the $^{117,119}Sn$ satellites in the case of the 1:1 complex) if the ^{105}Pd hyperfine coupling had been resolvable.

The frozen-solution spectra show only a small degree of anisotropy, and only in the case of the 1:1 Pd complex is the

Table II. ESR Parameters of the One-Electron-Reduction Products of $SnCl_4$ Adducts of $[M(S_2C_2O_2)]^{2-}$ (M = Ni, Pd, Pt)

complex	g	a, G[a]	line width, G	g_1	g_2	g_3	A_1[a]	A_2[a]	A_3[a]
$[Ni(S_2C_2O_2)_2SnCl_4]^{3-}$	2.0065	5.6	1.4	c			c		
$[Ni(S_2C_2O_2)_2(SnCl_4)_2]^{3-}$	2.0010	4.6	1.1	c			c		
$[Pd(S_2C_2O_2)_2SnCl_4]^{3-}$	2.0039	10.8	1.3	1.994	2.006	2.011	9	14	9.5
$[Pd(S_2C_2O_2)_2(SnCl_4)_2]^{3-}$	2.0032	5.1	1.9	c			c		
$[Pt(S_2C_2O_2)_2(SnCl_4)]^{3-}$	2.007	11.0[b]	3.5	1.973	2.011	2.016	−13[c]	23	23
$[Pd(S_2C_2O_2)_2(SnCl_4)_2]^{3-}$	1.9982	12.7[b]	6.2	c			c		

[a] Hyperfine coupling ($\times 10^{-4}$ cm^{-1}) estimated from spectral simulations. [b] Probably ^{195}Pt coupling (see text). [c] Anisotropy not well resolved. [d] Estimated by simulation (see text).

spectrum sufficiently well resolved to allow measurement of the principal g values (Figure 2). It was observed however that, in going from the 1:1 to the 1:2 Pd complex, the degree of anisotropy in the g values decreases substantially.

The magnitudes of the Sn coupling constants are similar to those found previously by other workers in complexes of trialkyl- or triaryltin cations with semiquinone or semidione radical anions[4-10] and in complexes of $SnCl_4$ with semiquinones ($a(^{117,119}Sn)$ = 11.4 G in the 1:1 adduct of $SnCl_4$ with 2,3,5,6-tetrachlorobenzosemiquinone[11]). This strongly supports Coucouvanis' postulate that the unpaired electron occupies a π-antibonding orbital on the dithiooxalate ligands.[1,2] The closeness of the g values to the free-electron value, and the small degree of anisotropy in the g values for the frozen solutions, is also indicative of an essentially ligand-based orbital for the unpaired electron (cf. $g_{\parallel} = 2.205$, $g_{\perp} = 2.081, 2.061$ for $[Ni(mnt)_2]^{3-}$ (mnt = maleonitriledithiolate, $[S_2C_2(CN)_2]^{2-}$) which is regarded as a Ni^I complex, with the unpaired electron residing in an essentially metal-based orbital).[12-14]

It has been suggested that the stabilizing effect of the $SnCl_4$ molecules on the one-electron reduction products is due to a lowering of the energy of a π-antibonding orbital on the dithiooxalate ligand.[1,2] Hence, in the 1:1 adducts, the unpaired electron would be expected to reside mainly on the dithiooxalate molecule, which is coordinated to the $SnCl_4$. In the 1:2 adducts, the π^* orbitals of both ligands would be lowered, and the electron would be expected to be delocalized over both of them. Thus the spin density near the Sn nucleus would be higher in the 1:1 than in the 1:2 complexes, and the Sn hyperfine coupling constants should reflect this trend. A decrease in the Sn coupling constants in going from the 1:1 to the 1:2 adducts is in fact observed (Table II).

Coucouvanis et al. reported that the reduction of the parent bis(dithiooxalato)nickelate(II) and -palladate(II) complexes is irreversible. In order to investigate this point further, and to find out whether the ESR spectrum of the one-electron-reduction products could be obtained under any conditions, we reinvestigated the cyclic voltammetry of these compounds. They showed highly irreversible reductions at about−2 V (Table I). Reduction of the nickel complex at the appropriate potential in the in situ ESR cell produced no ESR signal. Clearly, if a nickel(I) complex is produced under these conditions, it is extremely unstable.

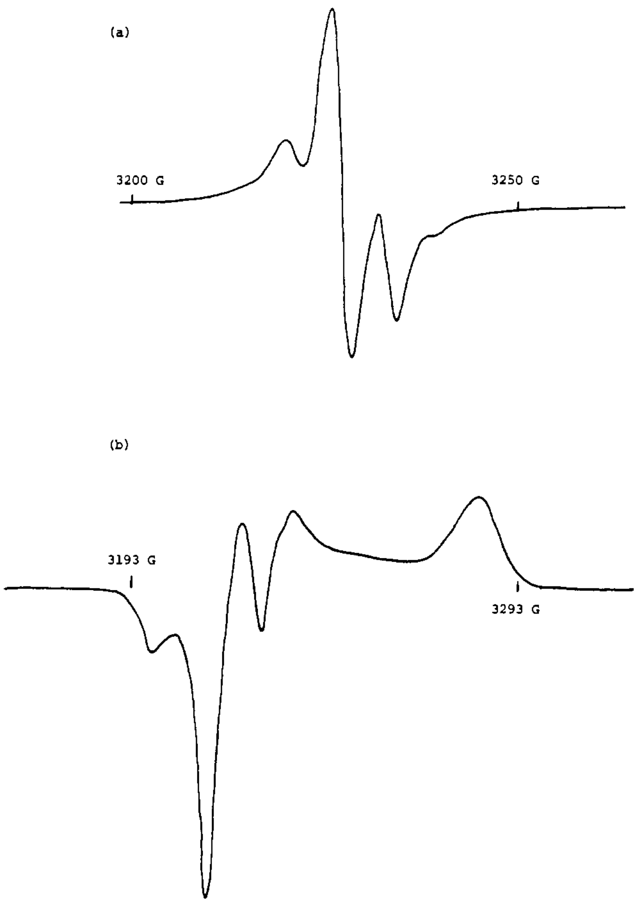

Figure 3. ESR spectra of $[Pt(S_2C_2O_2)_2(SnCl_4)]^{3-}$ electrogenerated in CH_2Cl_2 at 20 °C: (a) solution spectrum at 20 °C; (b) frozen-solution spectrum at −160 °C, 9.060 GHz.

The degree of stabilization of the ligand π^* orbitals was investigated by coordination of the α-diketone oxygens. For the Lewis acids $SnBr_4$, SnI_4, Ph_2SnCl_2, Ph_3SnCl, $TiCl_4$, $SiCl_4$, and $Cu(Ph_3P)_2$, no reversible reduction process was observed. The absence of reversible reduction for the 2:1 $SnBr_4$ and SnI_4 adducts has been reported previously.[1] No ESR spectra were observed when the $SnBr_4$, SnI_4, and $Cu(Ph_3P)_2$ adducts were reduced under the same conditions as those for the corresponding $SnCl_4$ complexes. Thus, apart from SnF_4,[1,2] there appear to be no other common Lewis acids capable of achieving the stabilization found for the $SnCl_4$ adducts.

(b) Pt Complexes. The cyclic voltammogram of a solution of $[Pt(S_2C_2O_2)_2]^{2-}$ showed no reduction process above −2 V. On addition of 1 mol equiv of $SnCl_4$ a reversible reduction was observed at −0.15 V. On further addition of slightly more than 1 mol equiv of $SnCl_4$ two reduction peaks were observed at −0.15 and −0.54 V. The first reduction showed reversible behavior when the scan was reversed before reaching the second reduction peak. This behavior is very similar to that observed for the corresponding Ni and Pd complexes and shows

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that 1:1 and 1:2 $SnCl_4$ adducts of the Pt complexes readily form in solution.

As in the case of the Ni and Pd complexes, in situ reaction of the $SnCl_4$ adducts in the ESR in situ cell at room temperature produced strong ESR signals consisting of a strong central line flanked by two satellites. When the solutions were frozen, the spectra became anisotropic, and evidence of the satellite lines remained in the frozen-solution spectrum. The solution spectrum for the 1:1 complex is shown in Figure 3a. In this case the satellite lines show a distinct inequality in intensity (particularly for the 1:1 complex), and the intensities are too high to be due to ^{117,119}Sn hyperfine coupling. The closest simulations of the observed spectra were obtained by assuming that the satellites are due to coupling with ^{195}Pt (33.7%, $I = {}^1/_2$), although the inequality in the intensities cannot be explained in this way. The frozen-solution spectrum of the 1:1 complex (Figure 3) appears to be axially symmetric, with the satellite structure resolved in the perpendicular region only. The coupling constant in this region is about 23×10^{-4} cm^{-1}, compared to 11.0×10^{-4} cm^{-1} in the isotropic solution spectrum, this value being obtained by a simulation of the spectrum with both the isotopes of platinum being included. Thus it appears that relative signs of the perpendicular and parallel components of the hyperfine interaction are of opposite sign (for example if a_{isotopic} was positive and $A_\perp$ positive, $A_\parallel$ would have to be negative to give $a_{\text{iso}} = 11 \times 10^{-4} = (2A_\perp + A_\parallel)/3 = (2 \times 23 \times 10^{-4} + (-13 \times 10^{-4}))/3$. This feature has been observed in other Pt radical anonic species.[15]

Registry No. I, 60240-65-5; $[Ni(S_2C_2O_2)_2]^{2-}$, 49871-88-7; $[Ni(S_2C_2O_2)_2(SnCl_4)]^{2-}$, 82374-22-9; $[Pd(S_2C_2O_2)_2]^{2-}$, 37578-58-8; $[Pd(S_2C_2O_2)_2(SnCl_4)]^{2-}$, 82374-23-0; $[Pd(S_2C_2O_2)_2(SnCl_4)_2]^{2-}$, 82374-24-1; $[Pt(S_2C_2O_2)_2]^{2-}$, 46165-21-5; $[Pt(S_2C_2O_2)_2(SnCl_4)]^{2-}$, 82374-25-2; $[Pt(S_2C_2O_2)_2(SnCl_4)_2]^{2-}$, 82374-26-3; $[Ni(S_2C_2O_2)_2(SnCl_4)]^{3-}$, 82374-27-4; $[Ni(S_2C_2O_2)_2(SnCl_4)_2]^{3-}$, 82444-31-3; $[Pd(S_2C_2O_2)_2(SnCl_4)]^{3-}$, 82374-28-5; $[Pd(S_2C_2O_2)_2(SnCl_4)_2]^{3-}$, 82444-32-4; $[Pt(S_2C_2O_2)_2(SnCl_4)]^{3-}$, 82374-29-6; $[Pt(S_2C_2O_2)_2(SnCl_4)_2]^{3-}$, 82444-33-5.

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Synthesis of (Silylamino)phosphines by the Wilburn Method[†]

Robert H. Neilson* and Patty Wisian-Neilson

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The importance of (silylamino)phosphines, e.g. $(Me_3Si)_2NPMe_2$, as reagents for the synthesis of organo-substituted phosphazene polymers[1] and other novel organophosphorus compounds[2,3] is now well established. Interest in these and related Si–N–P compounds as ligands in organometallic complexes[4] is also developing, and many other synthetic applications are likely to follow.

Most (silylamino)phosphines are prepared from commercially available reagents by a simple "one-pot" synthesis first utilized by Wilburn.[5,6] In earlier papers[4a,6] we have described the preparation of a few specific compounds on relatively small scales (50–100 mmol). Because of the synthetic value of these reagents, however, we report here the complete details for the convenient, large-scale (ca. 1–2 mol) synthesis of (silylamino)phosphines via the Wilburn procedure.

Table I. Physical and ^{31}P NMR Data for Some (Silylamino)phosphines, $(Me_3Si)_2NPRR'$

compd	R	R′	bp, °C (*P*, mm)	yield, %	$\delta(^{31}P)^a$
1	Me	Me	55–60 (4)	75	31.7
2	Et	Et	68–69 (1.6)	71	57.2
3	CH_2SiMe_3	CH_2SiMe_3	80–85 (0.3)	67	42.9
4	Me	Ph	90–95 (0.8)	81	37.6
5	Et	Ph	85–90 (0.1)	59	50.9

^{a} Chemical shifts downfield from external H_3PO_4, measured in $CDCl_3$ solution.

Experimental Section

Materials and General Procedures. All reactions and other manipulations were carried out under an atmosphere of dry nitrogen. Ethyl ether was distilled from calcium hydride prior to use. The following reagents were obtained from commercial sources: PCl_3, $PhPCl_2$, $(Me_3Si)_2NH$, *n*-BuLi, MeMgBr, and EtMgBr. The silylmethyl Grignard Me_3SiCH_2MgCl was prepared as needed according to the published procedure.[7]

Preparation of [Bis(trimethylsilyl)amino]dimethylphosphine (1). A 5-L, three-necked flask equipped with a paddle stirrer, a N_2 flow, and a 500-mL addition funnel was charged with $(Me_3Si)_2NH$ (1.0 mol, 209 mL) and Et_2O (ca. 1.0 L). One bottle of *n*-BuLi (ca. 1.0 mol, 2.0 M in hexane) was transfered to the addition funnel under nitrogen pressure by means of a flexible, double-ended syringe needle[8] and was added dropwise to the stirred silylamine solution at 0 °C. The addition funnel was then washed with ca. 30 mL of ether and charged with PCl_3 (1.0 mol, 87.2 mL). After the $LiN(SiMe_3)_2$ mixture was stirred at room temperature for ca. 90 min, it was cooled to −78 °C, and the PCl_3 was added dropwise. Upon completion of the addition, the −78 °C bath was removed. During the warm-up period the orange solution gradually turned white as LiCl precipitated. After ca. 1 h the mixture was cooled to 0 °C, and the addition funnel was again rinsed with Et_2O. Two bottles of MeMgBr (ca. 2.0 mol, 3.0 M in Et_2O) were transfered via the double-ended needle to the addition funnel and added dropwise to the stirred reaction mixture at 0 °C over ca. 2 h. The mixture was stirred for 3 h and then allowed to stand overnight at room temperature. Under a stream of N_2, the supernatant solution was decanted into a large one-necked flask. The solids were washed with two 500-mL portions of Et_2O, and the washings were added to the first decantate. Most of the solvent was removed under reduced pressure, and ca. 500 mL of hexane was added to facilitate precipitation of the remaining Grignard salts. Filtration under N_2 followed by solvent removal left a viscous orange residue. Distillation through a short- or semishort-path distilling head gave $(Me_3Si)_2NPMe_2$[5,6] as a colorless liquid (166 g, 75% yield,[9] bp 55–60 °C (4 mm)) of high purity based on ^{1}H and ^{31}P NMR spectra.

Preparation of Other (Silylamino)phosphines. The same procedure using either commercial EtMgBr or freshly prepared Me_3SiCH_2MgCl[7] affords the corresponding dialkylphosphines $(Me_3Si)_2NPR_2$ (**2**, R = Et,[10] and **3**, R = CH_2SiMe_3[4a]). Alternatively, if $PhPCl_2$ is used in

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[†] Dedicated to the memory of Dr. James C. Wilburn, 1953–1981.

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(9) Yields up to 86% have been obtained by more careful and repeated washing of the solids.

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