Journal of Organometallic Chemistry, 210 (1981) 181—191
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

ORGANOSTIBINES AS LIGANDS. SYNTHESIS OF DIMETHYL(α-PICOLYL)STIBINE, DIMETHYL(8-QUINOLYL)STIBINE, AND (*R*; *S*)-METHYLPHENYL(8-QUINOLYL)STIBINE AND SOME TRANSITION METAL DERIVATIVES

ERIC SHEWCHUK and STANLEY BRUCE WILD *

Department of Physical and Inorganic Chemistry, University of Western Australia, Nedlands, Western Australia 6009 (Australia)

(Received November 26th, 1980)

Summary

The unsymmetrical mono-tertiary stibines dimethyl(α-picolyl)stibine (picstib), dimethyl(8-quinolyl)stibine (quinstib), and (*R*; *S*)-methylphenyl(8-quinolyl)-stibine (*R*; *S*-quinstib) have been synthesised and the square-planar complexes [MX_2(picstib)], [MX_2(quinstib)] (where M = Pd or Pt and X = Cl, Br, I or SCN) and [MCl_2(*R*; *S*-quinstib)] (where M = Pd or Pt) isolated. The thiocyanato derivatives display linkage isomerism. The octahedral complexes [$M(CO)_4$-(picstib)] and [$M(CO)_4$(quinstib)] have also been prepared from the metal hexacarbonyls and the appropriate ligands by UV irradiation in tetrahydro-furan.

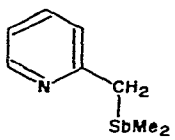
Introduction

In an earlier article we described the synthesis of *ortho*-phenylenebis-(dimethylstibine) and some of its transition metal derivatives [1]. We have now extended this work to include the unsymmetrical chelating mono-tertiary stibines dimethyl(α-picolyl)stibine (picstib) (I), dimethyl(8-quinolyl)stibine (quinstib) (II), and (*R*; *S*)-methylphenyl(8-quinolyl)stibine (*R*; *S*-quinstib) (III). They are the first chelating tertiary stibines containing a heterocyclic nitrogen ring. Analogous and related primary, secondary, and tertiary phosphorus and arsenic compounds have been known for some time, viz., dimethyl(α-picolyl)-arsine [2], tris(α-picolyl)phosphine [3], (8-quinolyl)arsine [4], dimethyl-(8-quinolyl)arsine [5] and its phenyl analogue [6], and (8-quinolyl)phosphine

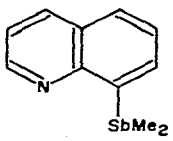
* Author to whom correspondence should be sent at his present address: Research School of Chemistry, The Australian National University, P.O. Box 4, Canberra, A.C.T. 2600 (Australia).

0022—328X/81/0000—0000/$02.50,

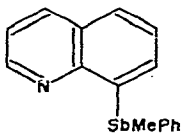
together with certain of its secondary (R = Me) and tertiary (R = Me) [7], (R = Ph) [6,7], derivatives.



(I)



(II)

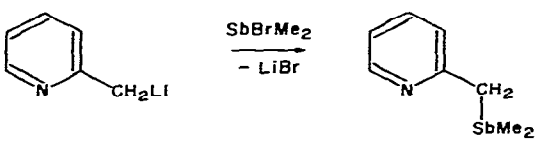


(III)

Results and discussion

Dimethyl(α-picolyl)stibine, (I)

The reaction between α-picolyllithium and bromodimethylstibine in diethyl ether afforded I in 33% yield (eq. 1). It is a pale yellow, air-sensitive liquid, b.p. 80—82°C/0.6 mmHg.



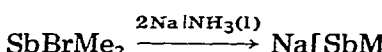
(1)

(I)

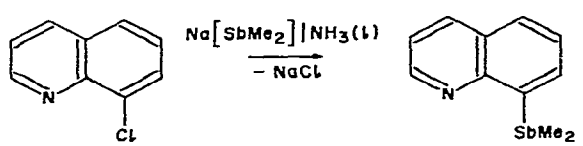
The ^{1}H NMR spectrum of I in $CDCl_3$ consisted of sharp singlets at δ 0.68 and δ 2.94 ppm for the antimony methyl and methylene protons, respectively, and a broad multiplet located between δ 6.74 and 7.60 ppm due to the aromatic protons. The methiodide exhibited a sharp singlet in $CDCl_3$ at δ 2.01 ppm due to the trimethylstibonium group: evidence of quaternisation of the heterocyclic nitrogen atom was not found. The mass spectrum of I is summarised in Scheme 1.

Dimethyl(8-quinolyl)stibine, (II)

Sodium dimethylstibide was generated in liquid ammonia and then reacted with 8-chloroquinoline as summarised in eqs. 2 and 3.



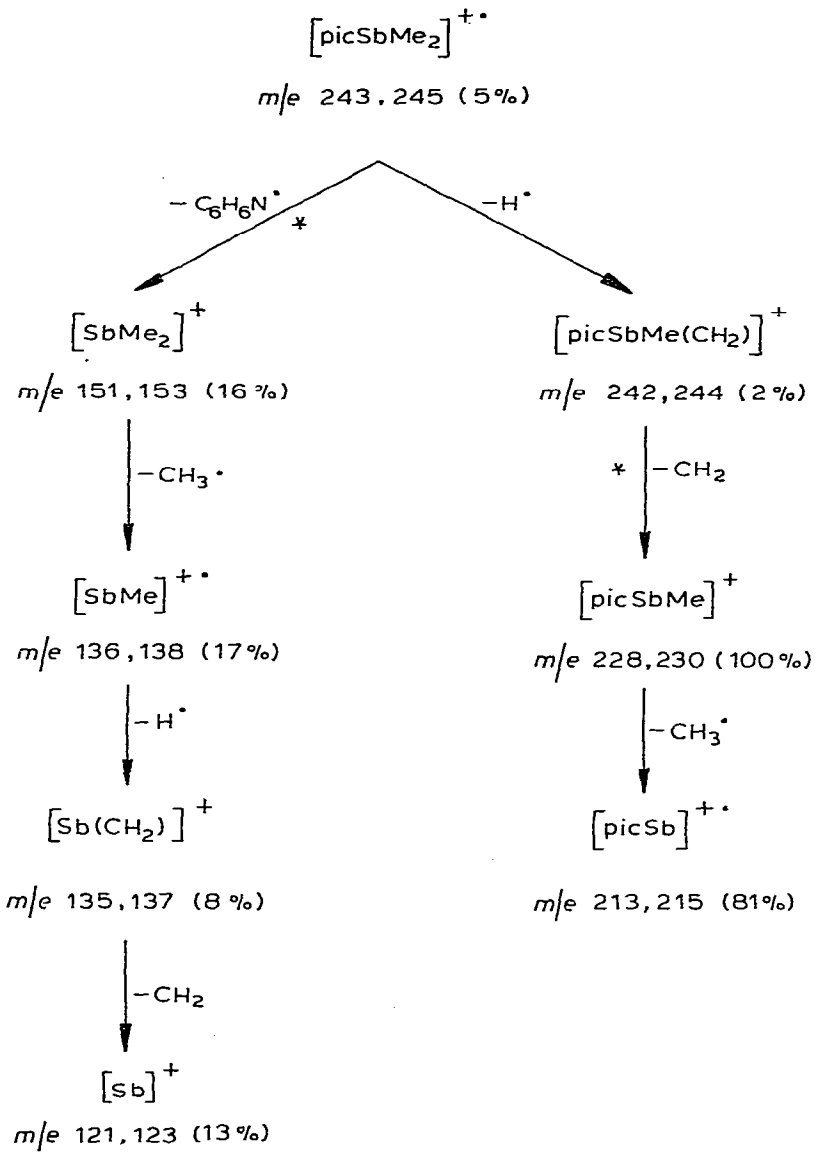
(2)



(3)

(II)

The product was obtained in 13% yield as a yellow-coloured, air-sensitive liquid, b.p. 106—107°C/0.5 mmHg. The principal by-product of the reaction was tetramethyldistibine (55% yield), which presumably arose by an oxidative coupling of the anion as suggested for its formation in the synthesis of *ortho*-phenylenebis(dimethylstibine) [1]. The ^{1}H NMR spectrum of II in $CDCl_3$ con-

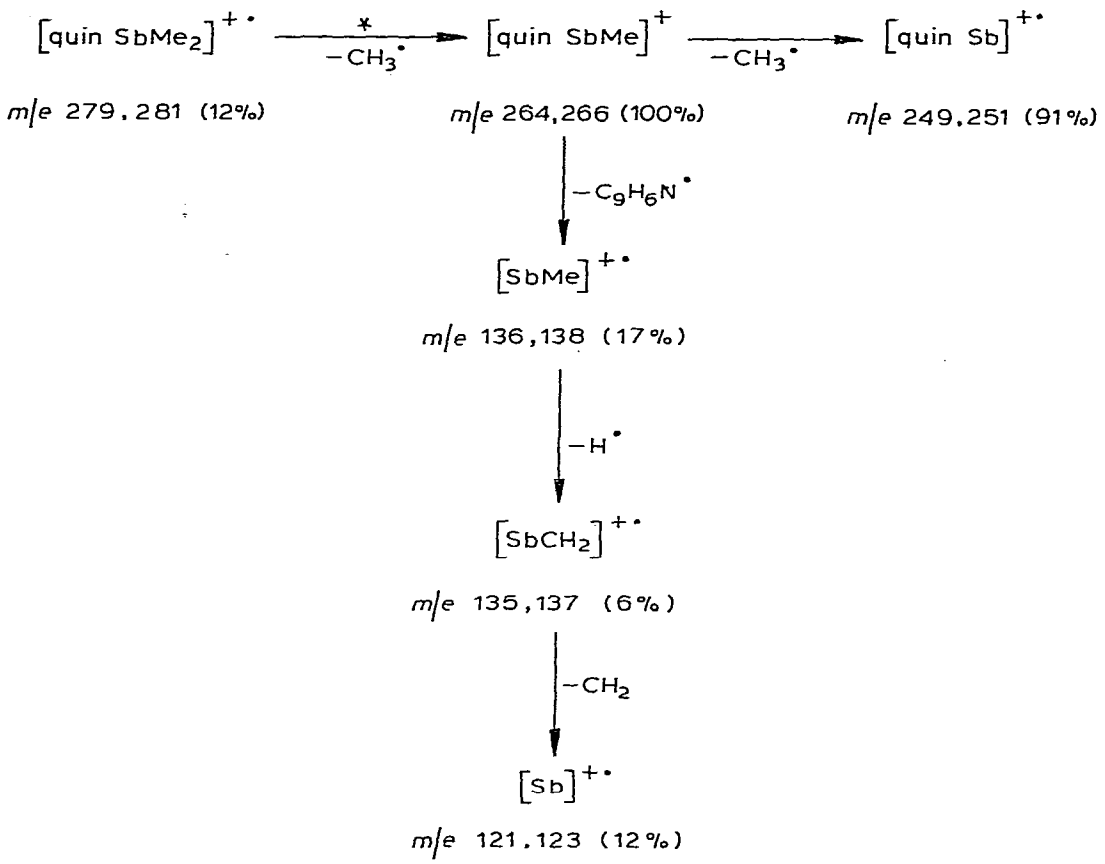


SCHEME 1

sisted of a sharp singlet at δ 0.96 ppm and a broad multiplet between δ 7.22 and 8.94 ppm due to the methyl and aromatic protons, respectively. Upon quaternisation with iodomethane the SbMe resonance was shifted downfield to δ 2.39 ppm. A molecular ion was observed in the mass spectrum of II although the base peak corresponded to $[M - Me]^+$. The fragmentation pattern of the antimony containing species is summarised in Scheme 2.

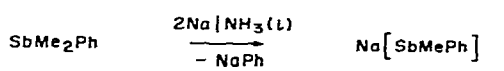
(R; S)-Methylphenyl(8-quinolyl)stibine, (III)

The reaction of sodium methylphenylstibide with 8-chloroquinoline in liquid



SCHEME 2

ammonia produced this asymmetric tertiary stibine in 45% yield:



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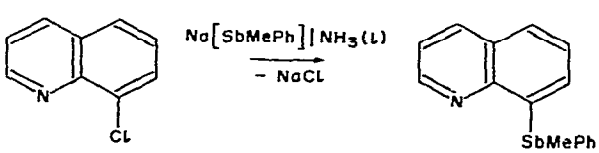
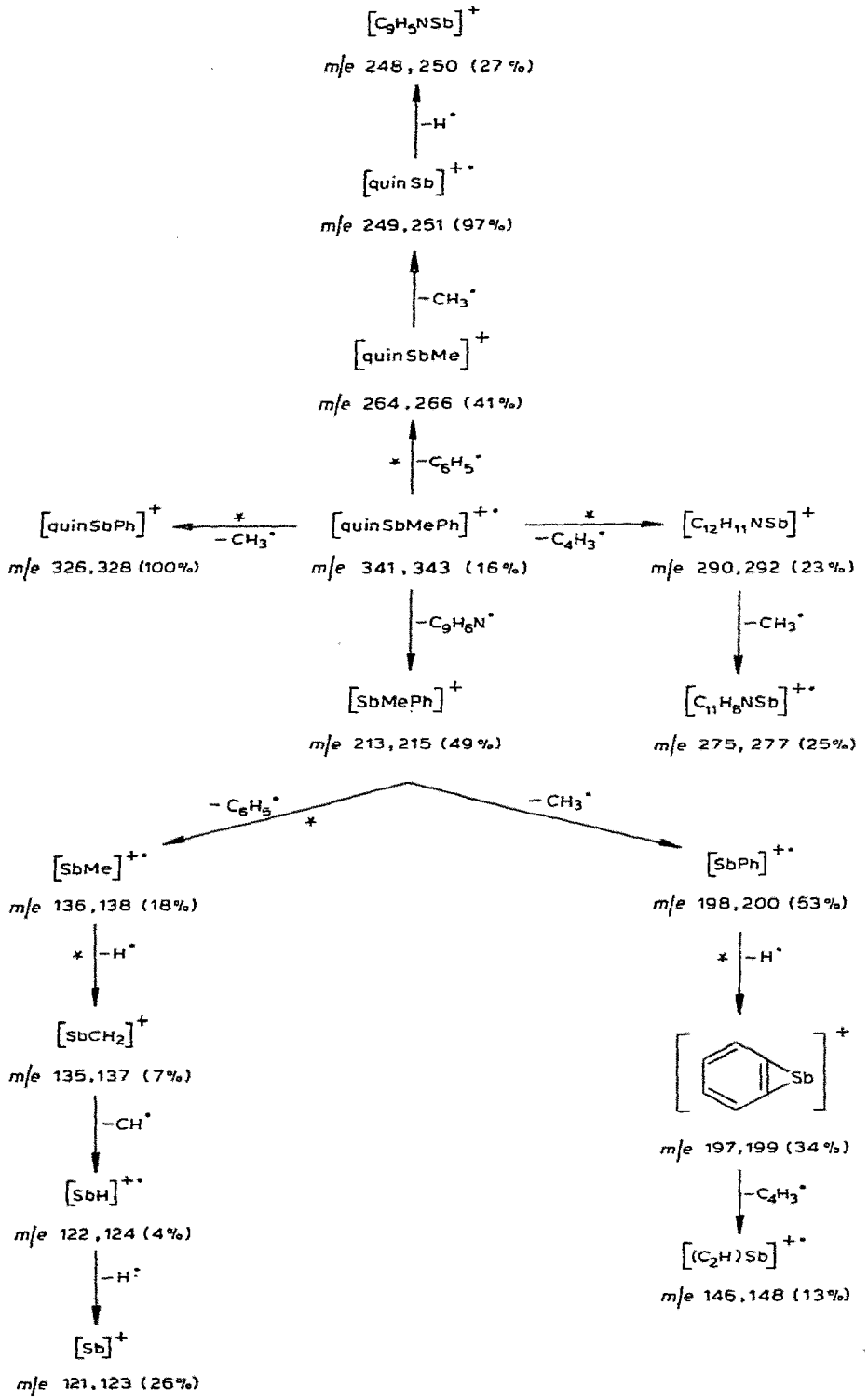


(III)

(5)

Compound III distilled as a viscous yellow oil, b.p. 156—157°C/0.2 mmHg. The SbMe resonance occurred at δ 1.18 ppm in $CDCl_3$ and the aromatic protons as a broad multiplet between δ 7.16 and 8.92 ppm. The methiodide displayed a resonance at δ 2.43 ppm due to the dimethylstibonium moiety. The mass spectrum of III is summarised in Scheme 3.


[C9H5NSb]+
m/e 248,250 (27%)
-H•
[quinSb]+•
m/e 249,251 (97%)
-CH3•
[quinSbMe]+
m/e 264,266 (41%)
* -C6H5•
[quinSbPh]+
* -CH3•
[quinSbMePh]+•
* -C4H3•
[C12H11NSb]+
m/e 326,328 (100%)
m/e 341,343 (16%)
m/e 290,292 (23%)
-C9H6N•
-CH3•
[SbMePh]+
[C11H8NSb]+•
m/e 213,215 (49%)
m/e 275,277 (25%)
- C6H5•
*
- CH3•
[SbMe]+•
[SbPh]+•
m/e 136,138 (18%)
m/e 198,200 (53%)
* -H•
* -H•
[SbCH2]+
Sb
m/e 135,137 (7%)
m/e 197,199 (34%)
-CH•
-C4H3•
[SbH]+•
[(C2H)Sb]+•
m/e 122,124 (4%)
m/e 146,148 (13%)
-H•
[Sb]+
m/e 121,123 (26%)

SCHEME 3

TABLE 1

PHYSICAL AND SPECTROSCOPIC PROPERTIES OF THE COMPLEXES [$M(CO)_4$(quinstib)] AND [$M(CO)_4$(picstib)]

Compound	Colour	m.p. (°C)	^{1}H NMR ($CDCl_3$, ppm)		IR ($CHCl_3$) ν(CO) (cm^{-1})
			δ(SbMe)	δ($SbCH_2$)	
[$Cr(CO)_4$(quinstib)]	yellow	130	1.09		2000s, 1902vs, 1891vs, 1864vs
[$Mo(CO)_4$(quinstib)]	yellow	119	1.08		2020s, 1921vs, 1908vs, 1972vs
[$W(CO)_4$(quinstib)]	pale yellow	128	1.18		2008s, 1900vs, 1890vs, 1868vs
[$Cr(CO)_4$(picstib)]	white	>150 (decomp.)	1.14	3.32	2007s, 1938vs, 1918vs, 1892vs
[$Mo(CO)_4$(picstib)]	pale yellow	220 (decomp.)	1.18	3.33	2024s, 1953vs, 1940vs, 1900vs
[$W(CO)_4$(picstib)]	white	180 (decomp.)	1.27	3.38	2012s, 1979vs, 1945vs, 1920vs

Bivalent palladium and platinum complexes

All three ligands readily formed the expected neutral complexes [MCl_2(bidentate)] (where M = Pd or Pt). These yielded [MX_2(bidentate)] (where X = Br, I, or SCN) upon metathesis with the appropriate sodium salt. The complexes are pale yellow to orange coloured diamagnetic solids which behaved as non-electrolytes in nitrobenzene. In the case of the derivatives of II coordination caused a 0.59 to 0.93 ppm downfield shift of the SbMe resonance compared to that found in the free ligand. The downfield shift was less in the complexes containing *R*; *S*-quinstib, consistent with the weaker σ-donor properties of the antimony donor atom in this molecule. The derivatives of picstib were not sufficiently soluble in the usual solvents for NMR studies.

The thiocyanato derivatives of II appear to display linkage isomerism for both metals. Two ν(CN) absorptions were observed in the infrared spectra of both pairs of complexes. The absorptions occurred at 2100 and 2035 cm^{-1} in the Nujol spectra of the palladium complexes, the peak at higher frequency being sharp and characteristic of an S-bonded thiocyanate [8]. In the case of platinum, the profile of the ν(CN) absorptions was similar, the two bands appearing at 2111 and 2040 cm^{-1}. The ν(CS) vibrations were not apparent due to strong ligand absorptions in the 700—900 cm^{-1} region. We propose that the S-thiocyanoto ligand is *trans* to the donor nitrogen atom in these complexes, as found in the structure of [Pd(NCS)(SCN){$Ph_2P(CH_2)_3NMe_2$}] [9]. Only the platinum thiocyanate of picstib could be isolated: the compound exhibited a single sharp absorption at 2110 cm^{-1}, which could not be resolved, suggesting S-bonded thiocyanato ligands only in this complex. However, it is appreciated that the nature of thiocyanate bonding is complicated in complexes of this type, being a function of electronic and steric factors operating within the molecule, as well as solvent effects [8].

The electronic absorption spectra of the dichloropalladium derivatives of the three ligands were recorded in dimethylformamide solution. The spectrum of [$PdCl_2$(quinstib)] contained bands centred at 24 800 (ϵ 700), 30 600 (ϵ = 5000), and 31 600 cm^{-1} ($\epsilon > 8000$). The lowest energy band is a *d*—*d* transition and its position and intensity may be compared to that found for the corresponding derivative of *ortho*-phenylenebis(dimethylstibine) [1]. In the case of [$PdCl_2$(picstib)] the transition occurs in a similar region of the spectrum [λ_{max} = 24 560 (ϵ = 1250)], but the ligand *R*; *S*-quinstib appears to have a lower ligand field strength in the same situation [λ_{max} = 23 850 (ϵ = 2130)] consistent with the chemical shift data cited earlier.

Zerovalent chromium, molybdenum, and tungsten complexes

The substitution complexes [$M(CO)_4$(quinstib)] and [$M(CO)_4$(picstib)] (where M = Cr, Mo, or W) were obtained by ultraviolet irradiation of the metal hexacarbonyl with one equivalent of the appropriate ligand in tetrahydrofuran solution. The complexes were isolated as crystalline solids (Table 1). A downfield shift of the SbMe resonance compared to the free ligand was observed in the ^1H NMR spectrum of each compound. However, consistent with the greater electron density on the metal atom in these systems the shifts were less than those observed in the corresponding derivatives of Pd^{II} and Pt^{II}. The infrared spectra of the tetracarbonyls in chloroform solution contained four ν(CO)

absorptions ($3A' + A''$) in agreement with the C_s local symmetry of the octahedral complexes. The physical and spectroscopic properties of the compounds are summarised in Table 1.

The metal carbonyls were sufficiently volatile for their mass spectra to be recorded. Each complex gave a molecular radical cation in the gas phase. The abundance of the molecular ions was low except in the case of $[W(CO)_4$-(picstib)] where 48% of the total ion current was carried by the molecular species. In this case successive losses of CO from the molecular ion were clearly observed leading to $[WL]^+$, the base peak in the spectrum. However, the base peak in the quinstib derivatives corresponded to $[L - Me]^+$.

Experimental

The preparation of the ligands and their metal derivatives were carried out in a nitrogen atmosphere using the Schlenk technique. Microanalyses were performed by the Australian Microanalytical Service, Melbourne and by Alfred Bernhardt, Max-Planck Institut, Mülheim, Germany. The ^1H NMR spectra were recorded at 60 MHz (35°C) using a Varian A-60 spectrometer; chemical shifts are quoted relative to tetramethylsilane as internal standard. The mass spectra were determined using a Varian MAT CH4 mass spectrometer. Molecular weights were determined by comparison with AR azobenzene in chloroform solution using the Signer method of isothermal distillation.

Dimethyl(α-picolyl)stibine, (I). A solution of α-picoline (15 g) in diethyl ether (30 ml) was added to a solution of phenyllithium [prepared from bromobenzene (25.7 g) and lithium pieces (2.24 g) in diethyl ether (200 ml)] over a period of 1 h. The resulting solution of α-picolyllithium was added slowly to a stirred suspension of $SbBrMe_2$ (32.9 g) [10] in the same solvent (100 ml). The lithium reagent initially produced a yellow colouration in the reaction mixture but this turned to an orange-yellow towards the end of the addition. The final reaction mixture was heated under reflux for 2 h, cooled to 0°C, and then hydrolysed with water (150 ml). The organic layer was separated, dried with $MgSO_4$, and distilled. After removal of the solvent the first fraction, b.p. 47—48°C/0.6 mmHg, was shown to be tetramethyldistibine (10.3 g, 30%) and the second, b.p. 80—82°C/0.6 mmHg after redistillation, the desired product (11 g, 32%). (Found: C, 39.5; H, 4.9; Sb, 49.8. Calcd. for $C_8H_{12}NSb$: C, 39.4; H, 5.0; Sb, 49.9%). ^1H NMR ($CDCl_3$): δ 0.68 (s, 6, SbMe), 2.94 (s, 2, $SbCH_2$—), 6.74—7.60 ppm (br m, 4, aromatics). Dissolution of the tertiary stibine in iodomethane afforded in a short time colourless crystals of the corresponding methiodide, which were recrystallised from acetone. (Found: C, 28.4; H, 3.9. Calcd. for $C_9H_{15}INSb$: C, 28.0; H, 3.9%). δ(SbMe): 2.01 ppm ($CDCl_3$).

Dimethyl(8-quinolyl)stibine, (II). The addition of sodium pieces (6.8 g) to a stirred suspension of $SbBrMe_2$ (34.4 g) in liquid ammonia (400 ml, distilled off Na) produced a deep red solution of $Na[SbMe_2]$. The reaction mixture was stirred for 1 h and then 8-chloroquinoline (19.6 g) was gradually added. At the end of the addition the reaction mixture was pale yellow-red in colour. The ammonia was allowed to evaporate off. Diethyl ether (300 ml) was added and the mixture heated under reflux for two hours. The mixture was then cooled to 0°C and water (200 ml) cautiously added. The organic layer was separated,

dried over $MgSO_4$, and distilled. After removal of the solvent two higher boiling fractions were collected: (i), b.p. 45—46°C/0.5 mmHg, tetramethyldistibine (18.2 g, 55%) and (ii), b.p. 106—107°C/0.5 mmHg, the desired product as a yellow coloured air-sensitive liquid (4.3 g, 13%). (Found: C, 47.5; H, 4.2; Sb, 43.0. Calcd. for $C_{11}H_{12}NSb$: C, 47.2; H, 4.3; Sb, 43.5%). ^1H NMR spectrum ($CDCl_3$): δ 0.96 (s, 6, SbMe), 7.22—8.94 ppm (br m, 6, aromatics). The methiodide was obtained as pale yellow needles from acetone, m.p. 208—209°C. (Found: C, 34.1; H, 3.6. Calcd. for $C_{12}H_{15}INSb$: C, 34.2; H, 3.6%). δ(SbMe): 2.39 ppm ($CDCl_3$).

Dimethylphenylstibine. A solution of phenylmagnesium bromide [prepared from bromobenzene (31.2 g) and magnesium turnings (5.5 g) in diethyl ether (400 ml)] was added over 1 h to a stirred suspension of $SbBrMe_2$ (46.1 g) in the same solvent (300 ml). The reaction mixture was heated under reflux for 1 h, cooled to 0°C, and then carefully hydrolysed with water (300 ml). The organic layer was separated, dried over $MgSO_4$, and distilled. The solvent was removed at 15 mmHg and the remaining material as follows: (i), b.p. 43—44°C/0.26 mmHg (22.6 g, 49.6%), the desired product (lit. [11] b.p. 112°C/16—18 mmHg). (Found: C, 41.7; H, 4.7; Sb, 53.2. Calcd. for $C_8H_{11}Sb$: C, 43.0; H, 4.8; Sb, 53.2%). ^1H NMR spectrum ($CDCl_3$): δ 0.79 (s, 6, SbMe), 7.0—7.3 ppm (m, 5, aromatics), and (ii) b.p. 103—104°C/0.2 mmHg (10.2 g, 17.6%) methyldiphenylstibine (lit. [11] b.p. 174—177°C/16—18 mmHg). (Found: C, 53.5; H, 4.5; Sb, 42.1. Calcd. for $C_{13}H_{13}Sb$: C, 53.7; H, 4.5; Sb, 41.9%). ^1H NMR spectrum ($CDCl_3$): δ 0.97 (s, 3, SbMe), 6.6—7.2 ppm (m, 10, aromatics).

(R; S)-Methylphenyl(8-quinolyl)stibine, (III). A solution of Na[SbMePh] was prepared from $SbMe_2Ph$ (8.3 g) [10] and sodium (1.67 g) in liquid ammonia (300 ml, distilled off Na). The deep red solution was stirred for 1.5 h, ammonium bromide (3.54 g) added, and then 8-chloroquinoline (5.91 g). The ammonia was allowed to boil off and the colourless residue extracted with boiling diethyl ether (300 ml) for one hour. The mixture was then cooled to 0°C and water (200 ml) added. The organic layer was separated, dried in the usual way and distilled. The product distilled as a viscous, yellow coloured, air sensitive oil, b.p. 156—157°C (0.2 mmHg) (5.5 g, 45%). (Found: C, 56.5; H, 3.9; Sb, 36.0. Calcd. for $C_{16}H_{14}NSb$: C, 56.2; H, 4.1; H, 35.6%). ^1H NMR ($CDCl_3$): δ 1.18 (s, 3, SbMe), 7.16—8.92 ppm (br m, 11, aromatics). The corresponding methiodide had m.p. 160°C (from dichloromethane/diethyl ether). (Found: C, 43.0; H, 3.7. Calcd. for $C_{17}H_{17}INSb$: 43.4; H, 3.7%). δ(SbMe): 2.43 ppm ($CDCl_3$).

Dichloro[dimethyl(8-quinolyl)stibine]palladium(II). Palladous chloride (0.21 g) was dissolved in warm methanol (30 ml) containing LiCl (0.35 g) and a solution of the ligand (0.33 g) in methanol (20 ml) added. Upon concentration the reaction mixture precipitated yellow crystals of the product. These were filtered off, washed with water and methanol, and dried in vacuo (0.38 g, 70%), m.p. 182°C. (Found: C, 29.2; H, 2.9. Calcd. for $C_{11}H_{12}Cl_2NPdSb$: C, 28.9; H, 2.6%). δ(SbMe): 1.83 ppm ($CDCl_3$). MW($CHCl_3$): Found, 444. Calcd. 458.

Metathesis of the chloro complex with the appropriate sodium salt afforded the corresponding bromo, iodo and thiocyanato derivatives in high yield. This was effected by dissolving the chloro compound in dichloromethane and shaking the solution with a six-fold excess of the sodium salt in water. The

organic layer was then separated, dried over $MgSO_4$, filtered, and evaporated to dryness to give the crude product, which was recrystallised from dichloromethane/methanol mixture ($PdBr_2$(quinstib)], orange crystals, m.p. 186—187°C. [Found: C, 24.6; H, 2.4. Calcd. for $C_{11}H_{12}Br_2NPdSb$: C, 24.2; H, 2.2%). δ(SbMe): 1.87 ppm ($CDCl_3$). [PdI_2(quinstib)], deep red crystals, m.p. 141°C (Found: C, 20.5; H, 2.1. Calcd. for $C_{11}H_{12}I_2NPdSb$: C, 20.6; H, 1.9%). δ(SbMe): 1.89 ppm ($CDCl_3$); [Pd(NCS)(SCN)(quinstib)], orange microcrystals, m.p. 177—178°C (Found: C, 31.5; H, 2.65. Calcd. for $C_{12}H_{12}N_2PdSSb$: C, 31.1; H, 2.4%). δ(SbMe): 1.45 ppm ($CDCl_3$). ν(CN): 2100, 2035 cm^{-1} (Nujol).

Dichloro[dimethyl(8-quinolyl)stibine]platinum(II). A solution of $K_2[PtCl_4]$ (0.34 g) in water (10 ml) was added dropwise to a stirred solution of quinstib (0.23 g) in ethanol (20 ml). Pale yellow crystals of the product deposited rapidly. These were isolated, washed with ethanol (95%), and dried (0.38 g, 85%), m.p. 206—207°C. (Found: C, 24.8; H, 2.3. Calcd. for $C_{11}H_{12}Cl_2NPtSb$: C, 24.2; H, 2.2%). δ(SbMe): 1.77 ppm ($CDCl_3$). MW ($CHCl_3$): Found, 540. Calcd. 546.

Metathesis of the chloro complex with the appropriate sodium salts yielded the following derivatives, which were isolated as described for the palladium complexes. [$PtBr_2$(quinstib)], honey yellow crystals, m.p. 218°C. (Found: C, 20.6; H, 1.9. Calcd. for $C_{11}H_{12}Br_2NPtSb$: C, 20.8; H, 1.9%). δ(SbMe): 1.78 ppm ($CHCl_3$). [PtI_2(quinstib)], orange-yellow crystals, m.p. 204—206°C (decomp.). (Found: C, 18.6; H, 1.7. Calcd. for $C_{11}H_{12}I_2NPtSb$: C, 18.1; H, 1.7%). δ(SbMe): 1.80 ppm ($CDCl_3$). [Pt(NCS)(SCN)(quinstib)], yellow crystals, m.p. 195°C. (Found: C, 26.6; H, 2.3. Calcd. for $C_{12}H_{12}N_2PtSSb$: C, 26.4, H, 2.1%). δ(SbMe): insufficiently soluble. ν(CN): 2111, 2040 cm^{-1} (Nujol);

Dichloro[(R;S)-methylphenyl(8-quinolyl)stibine]palladium(II). Prepared in the same way as the quinstib analogue; bright yellow crystals, m.p. 157°C (Found: C, 37.1; H, 2.8. Calcd. for $C_{15}H_{14}Cl_2NPdSb$: C, 37.0; H, 2.7%). δ(SbMe): 1.43 ppm ($CDCl_3$).

Dichloro[(R;S)-methylphenyl(8-quinolyl)stibine]platinum(II). Prepared in the same way as the quinstib analogue; pale yellow crystals, m.p. 165°C (Found: C, 31.6; H, 2.4. Calcd. for $C_{15}H_{14}Cl_2NPtSb$: C, 31.6; H, 2.3%). δ(SbMe): 1.57 ppm ($CDCl_3$).

Dihalogeno[dimethyl(α-picolyl)stibine]palladium(II). These were prepared in the usual way; they were not sufficiently soluble for NMR spectra to be recorded. [$PdCl_2$(picstib)], bright yellow crystals, m.p. 158—159°C. (Found: C, 22.7; H, 3.0. Calcd. for $C_8H_{12}Cl_2NPdSb$: C, 22.8; H, 2.9%). [$PdBr_2$(picstib)], orange yellow crystals, m.p. 175—176°C. (Found: C, 18.5; H, 2.2. Calcd. for $C_8H_{12}Br_2NPdSb$: C, 18.8; H, 2.4%). [PdI_2(picstib)], orange red crystals, m.p. 147—149°C (decomp.) (Found: C, 15.9; H, 2.0. Calcd. for $C_8H_{12}I_2NPdSb$: C, 15.9; H, 2.0%).

Dihalogeno[dimethyl(α-picolyl)stibine]platinum(II). These were obtained in the same way as their quinstib analogues. The complexes were not sufficiently soluble for NMR studies. [$PtCl_2$(picstib)], pale yellow crystals, m.p. 211—212°C (Found: C, 19.0; H, 2.5. Calcd. for $C_8H_{12}Cl_2NPtSb$: C, 18.8; H, 2.4%). [$PtBr_2$(picstib)], yellow crystals, m.p. 206—207°C (decomp.) (Found: C, 16.5; H, 2.2 Calcd. for $C_8H_{12}Br_2NPtSb$: 16.1; H, 2.0%). [PtI_2(picstib)], deep yellow crystals, m.p. 198—199°C. (Found: C, 13.7; H, 1.7. Calcd. for $C_8H_{12}I_2NPtSb$:

C, 13.9; H, 1.8%). [$Pt(SCN)_2$(picstib)], yellow crystals, m.p. 143—144°C. (Found: C, 21.5; H, 2.1. Calc. for $C_{10}H_{12}N_2PtSSb$: C, 21.6; H, 2.2%). ν(CN): 2110 cm^{-1} (Nujol).

Tetracarbonyl[dimethyl(8-quinolyl)stibine]metal(0) and tetracarbonyl-[dimethyl(α-picolyl)stibine]metal(0) (where metal = chromium, molybdenum, or tungsten). The general procedure for the preparation of these complexes was as follows. The metal hexacarbonyl and one equivalent of the appropriate ligand were dissolved in tetrahydrofuran and the solution irradiated with ultraviolet light until CO evolution ceased (ca. 2 h). The solvent was then removed and the product obtained from the residue by recrystallisation from toluene by the addition of n-hexane. The yields varied from 40—50%. Details of the physical and spectroscopic properties of the complexes are given in Table 1. Analyses: [$Cr(CO)_4$(quinstib)] (Found: C, 40.4; H, 2.6. Calcd. for $C_{15}H_{12}CrNO_4Sb$: C, 40.6; H, 2.7%). [$Mo(CO)_4$(quinstib)] (Found: C, 36.9; H, 2.3. Calcd. for $C_{15}H_{12}MoNO_4Sb$: C, 36.9; H, 2.5%). [$W(CO)_4$(quinstib)] (Found: C, 30.8; H, 2.1. Calcd. for $C_{15}H_{12}NO_4SbW$: C, 31.3; H, 2.1%). [$Cr(CO)_4$(picstib)] (Found: C, 35.5; H, 2.1. Calcd. for $C_{12}H_{12}CrNO_4Sb$: C, 35.2; H, 3.0%). [$Mo(CO)_4$-(picstib)] (Found: C, 31.6; H, 2.9. Calcd. for $C_{12}H_{12}MoNO_4Sb$: C, 31.8; H, 2.7%). [$W(CO)_4$(picstib)] (Found: C, 26.5; H, 2.4. Calcd. for $C_{12}H_{12}NO_4SbW$: C, 26.6; H, 2.2%).

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