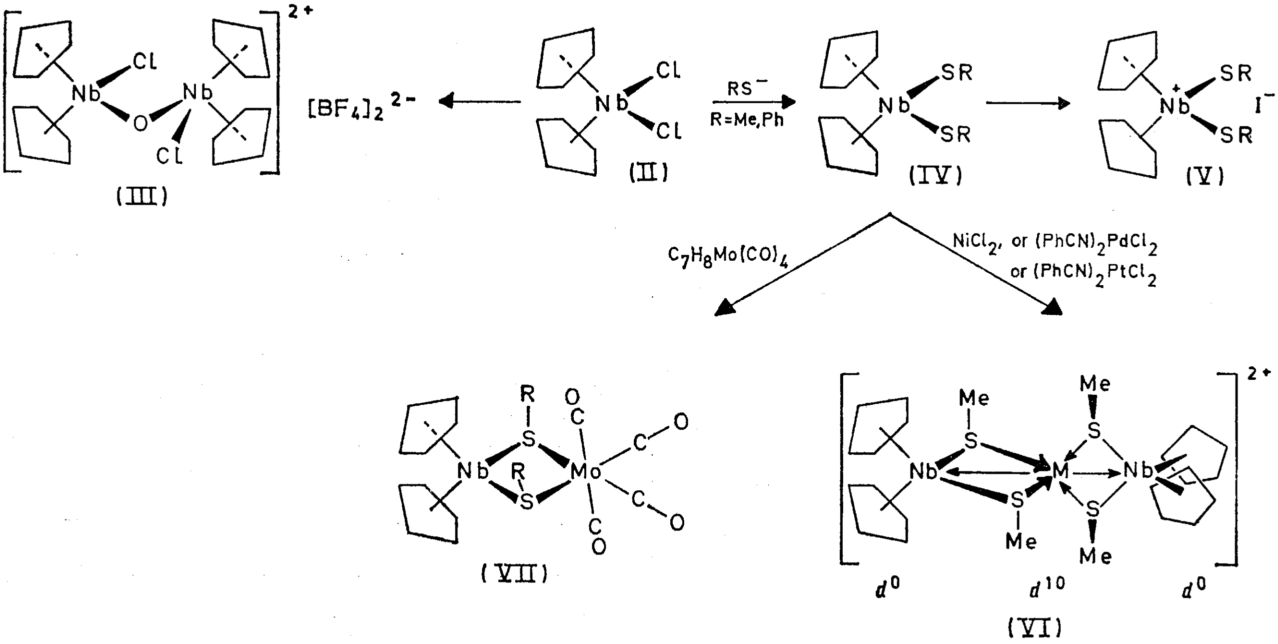
Transition Metal Complexes as Ligands: Preparation of Mixed Transition Metal Complexes of Niobium with Nickel, Palladium, Platinum, or Molybdenum

By **W. E. Douglas** and **M. L. H. Green**, Inorganic Chemistry Laboratory, South Parks Road, Oxford OX1 3QR

The dithio-derivatives $(\pi\text{-}C_5H_5)_2Nb(SR)_2$, R = Me or Ph and $[(\pi\text{-}C_5H_5)_2Nb(SMe)_2]^+A^-$ have been prepared. The bismethylthio-derivative forms the diamagnetic, trinuclear complexes $\{[(\pi\text{-}C_5H_5)_2Nb(SMe)_2]_2M\}^{2+}A_2^{2-}$, where M = Ni, Pd, or Pt. The bonding in the trinuclear complexes is discussed. A paramagnetic compound $(\pi\text{-}C_5H_5)_2Nb(SMe)_2Mo(CO)_4$ and a bridging-oxo-derivative $[(\pi\text{-}C_5H_5)_2NbCl]_2O]^+BF_4^-$ are also described.

DITHIO-DERIVATIVES of the type $(\pi\text{-}C_5H_5)_2M(SR)_2$, where M = Ti, Mo, or W have been shown to act as ligands to transition metals. For example the series of complexes $(\pi\text{-}C_5H_5)_2M(SR)_2Mo(CO)_4$, M = Ti, Cr, Mo, or W,[1-3] and the trinuclear complexes $[(\pi\text{-}C_5H_5)_2M(SMe)_2M'(SR)_2M(\pi\text{-}C_5H_5)_2]^{2+}A^{2-}$ (I, M = Mo or W, M' = Ni, Pd, or Pt)[4] have been isolated. The diamagnetic complexes (I) are thought to contain d^8, square-planar metal M' and the metals M are correspondingly described as d^2. It therefore seemed of interest to attempt to prepare complexes (I) where the metal M is niobium and, hence, there would be two electrons fewer in the system than for M = Mo or W. These studies and related results are described below; a preliminary account of part of this study has appeared.[5]



Chemical Studies.—At the outset of this work relatively few studies on the chemistry of the bis(π-cyclopentadienyl)niobium system had been described although several papers have subsequently appeared.[6] We looked for new or modified routes of preparation of the bis(π-cyclopentadienyl)niobium complexes and found that treatment of niobium pentachloride in 1,2-dimethoxyethane with thallium cyclopentadienide followed by extraction in air with concentrated hydrochloric acid to give a red-orange solution. Reduction of the solution with stannous chloride rapidly precipitates large brown crystals of the dichloride $(\pi\text{-}C_5H_5)_2NbCl_2$ (II) in 40% yield. The dichloride (II) is slightly soluble in hot concentrated hydrochloric acid and the aqueous acid solutions are readily oxidised, turning yellow-red. Addition of 40% tetrafluoroboric acid to a cold yellow-red solution gave orange crystals which analysis and crystal structure show to be the binuclear oxo-complex $\{[(\pi\text{-}C_5H_5)_2NbCl]_2O\}^{2+}[BF_4]_2^{2-}$ (III) (see the Scheme); full details of the crystal structure will be published elsewhere. Treatment of the dichloride (II) with

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[1] A. R. Dias and M. L. H. Green, *Rev. Port. Quim.*, 1969, **11**, 61.

[2] T. S. Cameron, C. K. Prout, G. V. Rees, M. L. H. Green, K. K. Joshi, G. R. Davies, B. T. Kilbourn, P. S. Braterman, and V. A. Wilson, *Chem. Comm.*, 1971, 14.

[3] P. S. Braterman, V. A. Wilson, and K. K. Joshi, *J. Chem. Soc.* (*A*), 1970, 191.

[4] A. R. Dias and M. L. H. Green, *J. Chem. Soc.* (*A*), 1971, 1951.

[5] W. E. Douglas, M. L. H. Green, C. K. Prout, and G. V. Rees, *Chem. Comm.*, 1971, 896.

[6] F. N. Tebbe and G. W. Parshall, *J. Amer. Chem. Soc.*, 1971, **93**, 3796; L. J. Guggenberger and F. N. Tebbe, *ibid.*, p. 5924.

methanethiol in the presence of base rapidly gives a deep purple-red solution from which deep red-purple, air-sensitive crystals may be isolated. The data given in the Table show the compounds to be the d^1, dithio-derivative $(\pi\text{-}C_5H_5)_2Nb(SMe)_2$ (IV). The phenylthio-analogue $(\pi\text{-}C_5H_5)_2Nb(SPh)_2$ is similarly prepared. The complexes (IV; R = Me or Ph) are soluble in dichloromethane and ethanol but only slightly soluble in light petroleum. Addition of iodine to dichloromethane solutions of the complex (IV; R = Me) causes immediate reaction and violet needles precipitate. The data in the Table show them to be the compound $[(\pi\text{-}C_5H_5)_2Nb(SMe)_2]^+I^-$ (V). The compound is soluble in water and the hexafluorophosphate salt $[(\pi\text{-}C_5H_5)_2Nb(SMe)_2]^+PF_6^-$ may be precipitated from aqueous solutions. The salts of the cation (V) are stable in air for periods of weeks.

Addition of a purple ethanol solution of the methylthio-derivative $(\pi\text{-}C_5H_5)_2Nb(SMe)_2$ to hydrated nickel dichloride in ethanol gives a dark brown solution from which brown salts of stoicheiometry $\{[(\pi\text{-}C_5H_5)_2Nb(SMe_2)]_2Ni\}^{2+}A_2^{2-},H_2O$ (VI), A = BF_4 or PF_6 were isolated.

Analytical and spectroscopic data

Compound	Colour	Analytical data, found (reqd.)		^{1}H n.m.r. data, τ(Hz) or e.s.r. data (G)
		% C	% H	
$\{[(\pi\text{-}C_5H_5)_2NbCl]_2O\}^{2+}[BF_4]_2^{2-}$ (III)	Orange	34·0 (34·0)	2·8 (2·8)	
$(\pi\text{-}C_5H_5)_2Nb(SMe)_2$ [a] (IV), R = Me)	Purple	45·4 (44·6)	4·8 (5·1)	$\langle g \rangle = 1{\cdot}991$, $A = 25{\cdot}1$ (10 lines).
$(\pi\text{-}C_5H_5)_2Nb(SPh)_2$ [b] (IV, R = Ph)	Purple-green	58·6 (59·9)	4·6 (4·6)	$\langle g \rangle = 1{\cdot}989$, $A = 30{\cdot}6$ (10 lines).
$[(\pi\text{-}C_5H_5)_2Nb(SMe)_2]^+PF_6^-$ (V)	Purple	31·5 (31·2)	3·4 (3·5)	3·25, **10**, *s*, $\pi\text{-}C_5H_5$; 6·93, **6**, *s*, Me($^6H_2\text{-}Me_2CO$).
$\{[(\pi\text{-}C_5H_5)_2Nb(SMe)_2]_2Ni\}^{2+}Cl_2^{2-},H_2O$ (VI)	Black			
$\{[(\pi\text{-}C_5H_5)_2Nb(SMe)_2]_2Ni\}^{2+}[BF_4]_2^{2-},H_2O$ (VI)	Brown-black	32·6 (32·6)	3·9 (3·9) [c]	—
$\{[(\pi\text{-}C_5H_5)_2Nb(SMe)_2]_2Ni\}^{2+}[PF_6]_2^{2-},H_2O$ (VI)	Brown-black	28·6 (28·8)	3·4 (3·3)	4·22, **20**, *s*, $\pi\text{-}C_5H_5$; 7·69, **12**, *s*, Me(SO_2).
$\{[(\pi\text{-}C_5H_5)_2Nb(SMe)_2]_2Pd\}^{2+}[PF_6]_2^{2-}$ (VI)	Red-purple	28·1 (28·0)	3·6 (3·1) [d]	3·38, **20**, *s*, $\pi\text{-}C_5H_5$; 6·67, **12**, *s*, Me(D_2O).
$\{[(\pi\text{-}C_5H_5)_2Nb(SMe)_2]_2Pt\}^{2+}[PF_6]_2^{2-}Me_2CO$ (VI)	Red-purple	27·4 (27·5)	3·2 (3·25) [e]	—
$\{[(\pi\text{-}C_5H_5)_2Nb(SMe)_2]_2Pt\}^{2+}[Cl]_2^{2-},2H_2O$ (VI)	Red-pruple	30·5 (30·8)	3·8 (3·9)	3·46, **20**, *s*, $\pi\text{-}C_5H_5$; 6·76, **12**, *t*($J_{Pt\text{-}H}$ 40·2), Me(D_2O).
$(\pi\text{-}C_5H_5)_2Nb(SMe)_2Mo(CO)_4$ (VII)	Green	36·7 (36·6)	3·5 (3·1) [f]	—

[a] $\mu_{eff} = 1{\cdot}71$ B.M.; $m/e = 441$; m.p. 170·5°; for $(\pi\text{-}C_5H_5)_2NbCl_2$ $\langle g \rangle = 1{\cdot}978$, $A = 35{\cdot}9$. [b] $m/e = 317$, m.p. 135—140° [c] $\chi_m = -607 \times 10^{-6}$ e.m.v. at 22°. [d] $\chi_m = -495 \times 10^{-6}$ e.m.v. at 20°. [e] $\chi_m = -492 \times 10^{-6}$ e.m.v. at 22°, *d*, 250°. [f] $\nu(C{\equiv}O) = 2043, 2001, 1983, 1966, 1895, 1860, 1798$ cm^{-1}.

The palladium and platinum analogues of the nickel cation (VI) are similarly prepared, see the Scheme. The complexes (VI; M = Ni, Pd or Pt) have been found to be diamagnetic (see the Table). Solutions of the salts of the cations (VI; M = Ni, Pd or Pt) in acetone or dimethyl sulphoxide are decomposed after *ca.* 15 min exposure in air. The crystal structure of the cation (VI; M = Ni) has been determined; the details are described elsewhere but the essentials are shown in the Scheme, in particular, the nickel is found to lie in an almost exactly symmetrical tetrahedral environment of the four sulphur atoms and the nickel–niobium distances are 2·78 Å.[5]

Addition of tetracarbonyl(bicyclo[2,2,1]heptadiene)-molybdenum to the methylthio-derivative (IV; R = Me) in toluene causes a precipitation of purple-green crystals. These were insoluble in many solvents except dichloromethane (sparingly), methanol, and dimethyl sulphoxide but solutions in these solvents steadily decompose. The crystals also decompose steadily in air (30 min) and they are involatile. It was not found possible to recrystallise or otherwise purify the compound. However consistent analysis of the initial crystals could be obtained and the data support the expected stoicheiometry for the product as the tetracarbonyl $(\pi\text{-}C_5H_5)_2Nb(SMe)_2Mo(CO)_4$ (VII). The i.r. spectra in the region 2100—1800 cm^{-1} (see the Table) show a resemblance to that of the analogous compounds $(\pi\text{-}C_5H_5)_2M(SPh)_2Mo(CO)_4$, M = Mo or W. The e.s.r. spectra of the compounds (II) and (IV) have been determined and the data is given in the Table. Each spectrum shows ten lines arising from coupling with the ^{93}Nb nucleus $I = 9/2$. For the dichloro-compound (II) no coupling with the chlorine nuclei was observed. The observed line widths of the components of the spectrum were found to be in good agreement with those predicted by the McConnell mechanism of line broadening.[7]

Dilute solutions of the compound (VII) in dichloromethane steadily decompose even in an inert atmosphere. Nevertheless it was possible to obtain an e.s.r. spectrum which showed ten components as expected (see the Table).

DISCUSSION

On the basis of the above evidence the structures for the complexes shown in the Scheme are suggested.

It has been proposed[8] that the bonding of the bent bis(π-cyclopentadienyl)metal system to other ligands involves essentially three orbitals which may be regarded as being little involved in the metal–cyclopentadienyl ring bonding. These three orbitals ψ_A, ψ_B, and ψ_C are shown in Figure 1. Crystal structure determinations on complexes $(\pi\text{-}C_5H_5)_2MX_2$, where M = Ti, Zr, V, Nb,

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[7] H. M. McConnell, *J. Chem. Phys.*, 1956, **25**, 709.

[8] J. C. Green, M. L. H. Green, and C. K. Prout, *Chem. Comm.*, 1972, 421, and references therein.

Mo, W, and Re and X may be a halogen or other one-electron ligand, suggest that, in those compounds where the metal is d^1 or d^2, these electrons are located in the ψ_A orbital which lies along the y-axis, and therefore it is this orbital which is the highest filled orbital.[8,9] It can be seen however that the ψ_A and ψ_B orbitals have the same symmetry with respect to the orbitals from the ligands X_2 and therefore the alternative arrangement, that is, with the ψ_B orbital being the highest filled orbital, could also occur. Since the ψ_A and ψ_B orbitals are normal to each other it is unlikely that the ligand orbitals would choose to interact equally with both orbitals but would prefer one to the other.

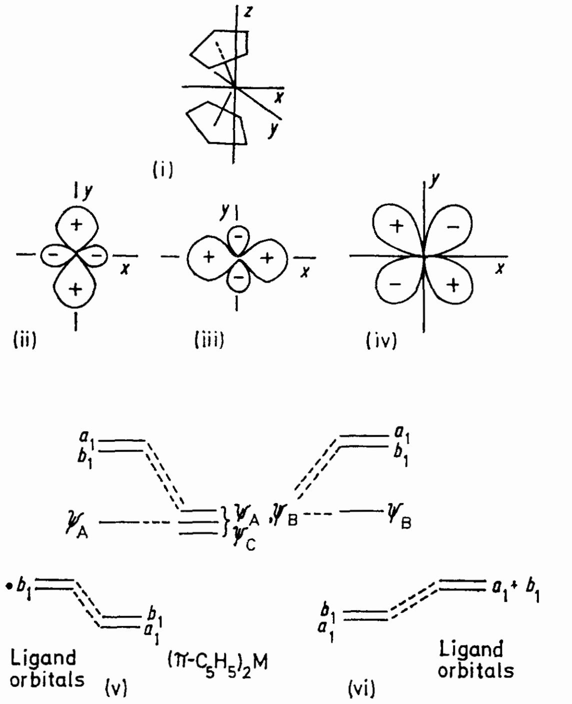

FIGURE 1 (i) Showing axes for the bent $(\pi\text{-}C_5H_5)_2M$ system. (ii) ψ_A orbital. (iii) ψ_B orbital. (iv) ψ_C (essentially d_{xy}) orbital. (v) M.O.'s of $(\pi\text{-}C_5H_5)_2MX_2$ resulting from interaction between the $(\pi C_5H_5)_2M$ system and the symmetric and anti-symmetric combinations of the π-bonding orbitals of X_2 giving an acute X–M–X angle, (ψ_A is ' non-bonding '). (vi) Ditto, but giving an obtuse X–M–X angle, (ψ_B is ' non-bonding ')

If the ligand orbitals a_1 and b_1 overlap strongly with the ψ_A and ψ_C orbitals respectively then the X–M–X angle would be obtuse whilst overlap with the ψ_B and ψ_C orbitals would give rise to an acute angle, see Figure 1 (V), VI).

By analogy with the X–M–X angles found in the d^1 complexes $(\pi\text{-}C_5H_5)_2V(SPh)_2$, $(\pi\text{-}C_5H_5)_2NbCl_2$, and $[(\pi\text{-}C_5H_5)_2MoCl_2]^+$,[8] we predict that the S–Nb–S angle in the d^1 compound $(\pi\text{-}C_5H_5)_2Nb(SMe)_2$ would lie in the same region, *ca.* 85°. This would locate the unpaired electron in the ψ_A orbital as the highest filled orbital. The crystal structure of the cation $\{[(\pi\text{-}C_5H_5)_2Nb(SMe)_2]_2Ni\}^{2+}$ shows that the S–Nb–S angles are obtuse being 98·2° and that the Nb–Ni distance is short 2·78 Å.[5,9] If we consider for simplicity that the $(\pi\text{-}C_5H_5)_2Nb(SMe)_2$ part of the complex (VI; M = Ni) may be regarded as a ' ligand ' to the nickel, that is, as a functional group with a recognisable separate identity, then it appears from the obtuse S–Nb–S angle in compound (VI) that the order of the ψ_A and ψ_B orbitals has been reversed and that the ψ_B is now the highest orbital.

The local symmetry around the nickel atom in complex (VI; M = Ni) approximates to D_{2d} and a possible M.O. diagram for the NbS_2NiS_2Nb system can be drawn up (see Figure 2). This shows that the combinations $\psi_B + \psi_{B'}$ and $\psi_B - \psi_{B'}$ can interact with the d_{z^2}, 4s and the p_z, d_{xy} orbitals on the nickel respectively. Due to the favourable directional properties of the d_{z^2} orbital it seems that the $\psi_B + d_{z^2} + \psi_{B'}$ interaction is likely to form a strongly bonding system. The asymmetric combination $\psi_B - \psi_{B'}(B_2)$ would be expected to be weakly bonding or non-bonding. If the ψ_B and $\psi_{B'}$ orbitals are rather higher in energy than the nickel d_{z^2} orbital as seems likely, then the orbital will be largely nickel in character and will constitute a donor bond from the nickel to the niobium atoms. In which case the nearest formal description of the valency states of the nickel will be d^{10} whilst that of the niobium atoms will be d^0. If on the other hand the niobium ψ_B orbitals are of similar energy to that of the nickel d_{z^2} orbital then the Ni–Nb bond will be homo-polar and the nickel atom may be regarded as being tetrahedral d^6, while the

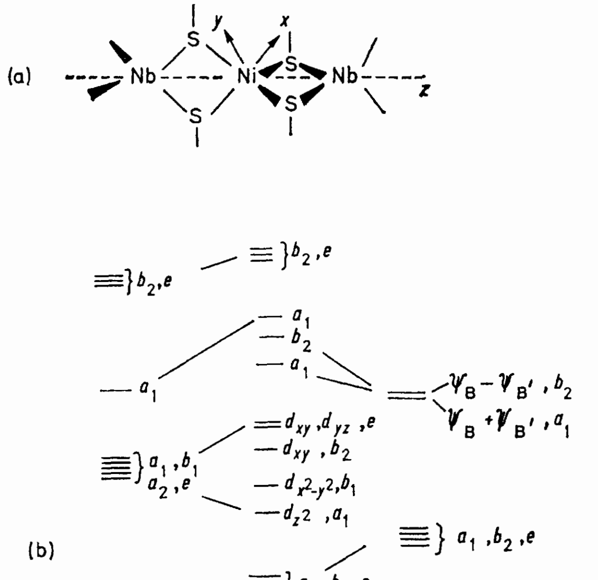

FIGURE 2 (a) Showing axes chosen for the NbS_2NiS_2Nb system (b) Possible M.O. diagram for the cation $\{[(\pi\text{-}C_5H_5)_2Nb(SMe)_2]_2Ni\}^{2+}$ assuming the local symmetry around the Ni atom is D_{2d} and that only the lone pair σ-electrons from sulphur and ψ_B, $\psi_{B'}$ orbitals are involved in bonding to the nickel

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[9] B. Denton and C. K. Prout, personal communication.

niobium atoms would be d^0. If there is no direct Nb–Ni bonding then a d^1–d^8–d^1 arrangement for the Nb–Ni–Nb system could arise. It would then be necessary to account for the observed diamagnetism of the compound in terms of antiferromagnetic coupling. Given the above alternatives we prefer the first formalism on general chemical grounds where the nickel is in the zero-valent state and the positive charge is considered to be localised largely on the d^0 niobium atoms. Further support for a donor bond from nickel to the niobium atom arises from the observation that the chemical shifts of the π-cyclopentadienyl hydrogen atoms of the complex (VI; M = Ni) is at lower field (*ca.* 1·0 τ) than the corresponding band for the cation (V). The same argument has been used to invoke Mo–Ti bonds in the compounds $(\pi\text{-}C_5H_5)_2Ti(SR)_2Mo(CO)_4$.[2] It is normally found that saturated sulphur ligands may not stabilise low-valent, electron-rich metal systems as well as ligands such as tertiary phosphines, since sulphur ligands are the poorer π-acceptors. The cations represent the first examples of zero-valent Ni, Pd, or Pt which might appear to be stabilised by sulphur ligands and in consequence the proposal of an essentially acceptor role for the niobium orbital in the nickel–niobium bonds seems reasonable. Formally we regard the $(\pi\text{-}C_5H_5)_2Nb(SMe)_2^+$ system as a 2 × 2-electron donor *via* the sulphur atoms and as a σ-acceptor *via* the niobium atom.

The i.r. spectrum of the molybdenum compound (VII) shows more than four bands assignable to $\nu(C\equiv O)$ and this is consistent with a symmetry lower than C_{2v}, that is with a *cis*-configuration for the methyl groups rather than a *trans*-configuration. The values of $\nu(C=O)$ of niobium compound are intermediate between the $\nu(C\equiv O)$ of the titanium and of the molybdenum analogues $(\pi\text{-}C_5H_5)_2M(SR)_2Mo(CO)_4$, M = Ti or Mo. This would be expected if there was a reduced acceptor role for the d^1 niobium than found for the d^0 titanium analogue.

EXPERIMENTAL

All preparations were carried out under nitrogen unless otherwise stated. Light petroleum is AnalaR (b.p. 30—40°). ^{1}H N.m.r. spectra were determined on a J.E.O.L. Co. instrument operating at 60 MHz at probe temperature. I.r. spectra were determined on a Perkin-Elmer 457 instrument in mulls and were calibrated with polystyrene. Magnetic susceptibility measurements were made by Dr D. F. Evans using the apparatus described.[10] Mass spectra were determined using a Perkin-Elmer MS9 spectrometer. E.s.r. spectra were measured on a Varian E4 instrument and calibrated using Fremy's salt $\langle g \rangle = 2{\cdot}0055 \pm 0{\cdot}00005$. 1,2-Dimethoxyethane was dried over calcium hydride.

Dichlorobis(π-cyclopentadienyl)niobium.—Niobium pentachloride (7·98 g) in dry 1,2-dimethoxyethane (140 ml) was treated with thallium cyclopentadienide (19·5 g) at −70°. The mixture was stirred for 6 h and then allowed to warm to room temperature and stirred for a further 8 h. The blue-grey mixture was then refluxed for 2 h. The solvent was removed under reduced pressure and the residue was extracted with hot, refluxing concentrated hydrochloric acid (5 × 50 ml) in the presence of air. The yellow-red extracts were concentrated to *ca.* 50 ml, cooled and water (50 ml) added. The white precipitate of thallium chloride was separated by filtration and the yellow-red filtrate was concentrated to 50 ml under nitrogen and treated with a solution of stannous chloride (3 g) in concentrated hydrochloric acid (10 ml). The mixture turned brown-green and after a few minutes long brown needles appeared. After another 2 h the brown crystals were separated, washed with deoxygenated hydrochloric acid and dried under reduced pressure. A further sample of the brown needles was obtained from the mother liquor. The brown needles were found to be the pure dichloride $(\pi\text{-}C_5H_5)_2NbCl_2$, yield *ca.* 35%.

μ-Oxo-bis[chlorobis(π-cyclopentadienyl)niobium] Tetrafluoroborate.—A suspension of the dichloride $(\pi\text{-}C_5H_5)_2NbCl_2$ (0·2 g) in concentrated hydrochloric acid (5 ml) was oxidised giving a deep red solution. This was concentrated until the solution was saturated at room temperature. The solution was filtered and tetrafluoroboric acid was added (40%, 2 ml). The solution was cooled at 0° for 48 h during which time orange crystals precipitated. These were separated, washed with dilute hydrochloric acid and dried under reduced pressure giving the pure *compound*, *ca.* 60%.

Diphenylthiobis-(π-cyclopentadienyl)niobium.— Ethanol (50 ml) was treated with sodium metal (0·25 g) and then thiophenol (3·5 ml). The dichloride $(\pi\text{-}C_5H_5)_2NbCl_2$ (2·0 g) was added to the mixture which was stirred and warmed to 60°. The purple solution was concentrated under reduced pressure and finally dried. The purple residue was extracted with dichloromethane and the purple extract was filtered and the filtrate was concentrated and treated with light petroleum. Green crystals precipitated and were separated from the pale red mother liquor. The crystals were recrystallised from dichloromethane–light petroleum giving the pure product, *ca.* 75%.

The methylthio-compound $(\pi\text{-}C_5H_5)_2Nb(SMe)_2$ was similarly prepared, *ca.* 90%.

Dimethylthiobis(π-cyclopentadienyl)niobium Salts.—The methylthio-compound $(\pi\text{-}C_5H_5)_2Nb(SMe)_2$ (0·6 g) in dichloromethane (20 ml) was treated with a solution of iodine (0·25 g) in dichloromethane (10 ml). Immediately violet needles separated, which were separated, washed with light petroleum and dried. Further purple needles were obtained from the concentrated mother liquor. Recrystallisation was from dichloromethane–light petroleum giving the pure violet iodide $[(\pi\text{-}C_5H_5)_2Nb(SMe)_2]^+I^-$, *ca.* 80%. The iodide was dissolved in water and the solution treated with an excess of ammonium hexafluorophosphate giving a violet precipitate. This was collected, dried *in vacuo* and finally recrystallised from dichloromethane–light petroleum, *ca.* 80%.

Bis[di-μ-methylthio-bis(π-cyclopentadienylniobium)]nickel Salts.—Hexa-aquonickel dichloride (0·42 g) in ethanol (40 ml) was added to a solution of the methylthio-derivative $(\pi\text{-}C_5H_5)_2Nb(SMe)_2$ (0·95 g) in ethanol (40 ml) with stirring. The mixture immediately became orange-brown. The solvent was removed under reduced pressure giving a black residue which was extracted with water. The orange-brown solution was filtered, concentrated, and treated with acetone. Brown needles separated which were washed with acetone and dried, *ca.* 75%. Analysis suggests the crystals to be the tetrachloronickelate salt $\{[(\pi\text{-}C_5H_5)_2Nb(SMe)_2]_2Ni\}^{2+}[NiCl_4]^{2-}$. An aqueous solution

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[10] D. F. Evans, *J. Chem. Soc.* (*A*), 1967, 1670.

of this compound was treated with excess of aqueous sodium tetrafluoroborate giving brown crystals. These were washed with a little water and then dissolved in acetone. Concentration of the filtered acetone extract under reduced pressure gave deep brown needles and the pure *tetrafluoroborate salt*. The salt could also be recrystallised from hot water. The *hexafluorophosphate salt* was similarly prepared using ammonium hexafluorophosphate solutions. It was less soluble in water.

Bis[di-μ-methylthio-bis(π-cyclopentadienyl)niobium]-palladium Salts.—Bis(benzonitrile)dichloropalladium (0·62 g) in dichloromethane was added to a solution of $(\pi\text{-}C_5H_5)_2Nb(SMe)_2$ (0·46 g) in dichloromethane (30 ml). The mixture was stirred for 2 h giving a green solution and a dark purple precipitate. The mixture was filtered and the residue was collected and washed with water giving a red solution and a green-brown residue, which was discarded. The filtrate was treated with excess of aqueous *hexafluorophosphate* ion giving a purple precipitate which was filtered, washed with water, dried, and finally recrystallised from acetone–water giving purple crystals, *ca.* 70%. The *tetrafluoroborate* salt was similarly prepared as purple needles from the red filtrate by addition of aqueous potassium tetrafluoroborate. The *dichloride* salt $\{[(\pi\text{-}C_5H_5)_2Nb(SMe)_2]_2Pd\}^{2+}[Cl^-]_2$ was prepared by addition of acetone to the concentrated red aqueous extract.

Bis[di-μ-methylthio-bis(π-cyclopentadienyl)niobium]-platinum Salts.—Dichlorobis(benzonitrile)platinum (0·36 g) in dichloromethane (15 ml) was added dropwise to bismethylthiobis(π-cyclopentadienyl)niobium (0·18 g) in dichloromethane (10 ml). The mixture was stirred for 4 h then filtered. The red precipitate was washed with dichloromethane until the washings were colourless and was then dried.

The residue was extracted with water (10 ml) and the extract was filtered. The filtrate was concentrated and acetone was added giving garnet needles of the *chloride* $\{[(\pi\text{-}C_5H_5)_2Nb(SMe)_2]_2Pt\}^{2+}Cl_2^{2-},2H_2O$, *ca.* 60%.

Treatment of aqueous solutions of the chloride salt with aqueous solutions of ammonium hexafluorophosphate gives a red precipitate which may be recrystallised from aqueous acetone. The red crystals were washed with water and dried giving the *hexafluorophosphate* salt $\{[(\pi\text{-}C_5H_5)_2Nb(SMe)_2]Pt\}^{2+}[PF_6]_2^{2-},Me_2CO$, *ca.* 80%.

Tetracarbonyl[di-μ-methylthio-bis(π-cyclopentadienyl)-niobium]molybdenum.— Tetracarbonyl(bicyclo[2,2,1]heptadiene)molybdenum (0·31 g) in toluene (10 ml) was added dropwise to bismethylthiobis(π-cyclopentadienyl)niobium (0·27 g) in toluene (100 ml) with stirring. Immediately a dark green precipitate formed and, after 1½ h, the solution was filtered giving a green crystalline residue. This was washed with toluene (3 × 25 ml) and dried *in vacuo* giving the pure compound, *ca.* 70%.

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