Chemical and Theoretical Comparison between Phosphido ($X = PR_2$) and Thiolato ($X = SR$) Bent Niobocenes of the Type $[Nb(cp)_2L(X)]$ [$L = CO$ or $P(OMe)_3$, cp = η-C_5H_5]. Structure of $[Nb(cp)_2(CO)(\mu\text{-}SEt)\{Fe(CO)_4\}]$†

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The hydrido complexes $[Nb(cp)_2H(L)]$ [$L = CO$ or $P(OMe)_3$, cp = η-C_5H_5] reacted with MeI to afford the iodo derivatives $[Nb(cp)_2L(I)]$ **1**. The reaction of **1** with Na(SEt) led to the terminal thiolato complexes $[Nb(cp)_2L(SEt)]$ **2**. Compounds **2** were used to bind the metal carbonyl fragments $Fe(CO)_4$ and $M(CO)_5$ from $[Fe_2(CO)_9]$ and $[M(CO)_5(thf)]$ (thf = tetrahydrofuran) respectively. The corresponding monothiolato-bridged complexes $[Nb(cp)_2L(\mu\text{-}SEt)\{M(CO)_n\}]$ **3** (M = Fe, $n = 4$; M = Mo or W, $n = 5$) were obtained only in the case of L = CO and no dibridged μ-SEt, μ-CO complex was formed. The new complexes **1**–**3** were characterized by IR, ^1H and ^{31}P NMR spectroscopies. The X-ray analysis of $[Nb(cp)_2(CO)(\mu\text{-}SEt)\{Fe(CO)_4\}]$ showed an *endo* position of the ethyl group with respect to the CO ligand bound to the niobium. The results of extended-Hückel molecular orbital (EHMO) conformational calculations carried out on the model complexes $[Nb(cp)_2(CO)(PMe_2)]$ and $[Nb(cp)_2(CO)(SMe)]$ are compared, and the importance of electronic and steric effects deduced. An explanation for the non-formation of dibridged μ-SEt, μ-CO complexes is attempted on the basis of EHMO and X-ray results.

The chemistry of bent niobocenes (Nb^{III}, d^2) of the type $[Nb(cp)_2(CO)X]$ (cp = η-C_5H_5; X = H, Cl, or Br) has been explored for a long time,[1-3] but only recently an iodo derivative of this type $[Nb(C_5H_4SiMe_3)_2(CO)I]$ has been reported.[4] The terminal phosphido compounds $[Nb(cp)_2L(PR_2)]$ [L = CO, R = Ph or Me;[5] L = PMe_2H or $P(OMe)_3$, R = Ph[6]] belong to this class of compounds. Analogous complexes with a niobium–sulfur bond, *i.e.* L = CO, X = SH[7] or SC(S)H,[8] have been derived from CS_2.

We have shown that the very easy reaction of niobophosphines $[Nb(cp)_2(CO)(PR_2)]$ (R = Ph or Me) with $[Fe_2(CO)_9]$ leads to a mixture of two complexes: a monobridged μ-PR_2 molecule without metal–metal interaction and a dibridged one (μ-PR_2, μ-CO) with a Nb–Fe bond.[5] The formation of these two complexes may be due to the high flexibility of the phosphido bridge as suggested by Carty *et al.*[9] This flexibility is illustrated by the large variation of the M–P–M′ angle which falls in the range 79–119° in phosphido-bridged monocyclopentadienyl (M = Fe or W)–metal carbonyl (M′ = Cr, Mo or W) bimetallics.[10] This range is still larger (75–129°) in phosphido-bridged bimetallics bearing a bent metallocene (M = Zr, Hf, Nb, Ta, Mo or W) and a metal carbonyl fragment (M′ = Cr, Mo, W, Mn or Fe).[5,6,11] In the thiolato-bridged dinuclear complexes derived from monocyclopentadienyl organometallics the range of bridging angles is very large (73–131°).[12] It is equal to 70–83° in dithiolato-bridged bent metallocenes of Ti^{IV}, Nb^{V}, Ta^{V}, Mo^{IV} and W^{IV}.[13] No structural data on monothiolato-bridged dinuclear niobocenes (Nb^{III}) are available.

The complexes of the type $[Nb(cp)_2(CO)(SR)]$ (R = alkyl or aryl) are closely related to the known metallophosphines $[Nb(cp)_2(CO)(PR_2)]$[5] (R = Me, Ph or Pr^i) for which operation of the 'transition-metal *gauche* effect' has been suggested.[14,15] Its efficient operation needs the presence of one well defined electronic lone pair on the metal and on the ligand, and is responsible for the high nucleophilicity of metallophosphines.[14] This electronic effect has been established by extended-Hückel molecular orbital (EHMO) calculations in the related hydrido metallophosphine $[Mo(cp)_2H(PH_2)]$ (Mo^{IV}, d^2).[11f] The conditions for an efficient operation of the *gauche* effect are apparently not assured in thiolato complexes $[Nb(cp)_2(CO)(SR)]$ because of the formal presence of two lone pairs at the sulfur atom. However, their repulsions with the metal lone pair as well as the steric effects induced by the R substituent of the thiolate group should result in a stable conformation. For terminal thiolato complexes derived from bent metallocenes, the chemical, structural and theoretical studies have been carried out only on the dithiolato derivatives $[M(cp)_2(SR)_2]$ (M = Ti, Nb, W or Mo; R = H, Me or Ph).[16]

We report here on the syntheses of iodo and monothiolato complexes derived from bent niobocene (Nb^{III}, d^2), $[Nb(cp)_2L(X)]$ [L = CO or $P(OMe)_3$; X = I or SEt], as well as on the results of EHMO calculations carried out on the niobophosphine $[Nb(cp)_2(CO)(PMe_2)]$ and on the terminal thiolato complex $[Nb(cp)_2(CO)(SMe)]$. The behaviour of the mononuclear compounds $[Nb(cp)_2L(SEt)]$ [L = CO or $P(OMe)_3$] towards co-ordination to the carbonyl fragments $Fe(CO)_4$ and $M(CO)_5$ (M = Mo or W) and the crystal structure of $[Nb(cp)_2(CO)(\mu\text{-}SEt)\{Fe(CO)_4\}]$ are also described.

Experimental

General.—All reactions were carried out under an argon atmosphere with the use of standard Schlenk techniques. The solvents and eluents were distilled under argon from sodium and benzophenone immediately before use. Column chromatographies were performed under argon with silica gel (70–230 mesh). Elemental (C, H) analyses were by the Service Central d'Analyse du CNRS (Gif sur Yvette).

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

Infrared spectra were recorded with a Nicolet 205 spectrophotometer, ^{1}H and ^{31}P NMR spectra on Bruker AC 200 spectrometers; chemical shifts are given in ppm relative to $SiMe_4$ (^{1}H) or (external) H_3PO_4 (^{31}P). The complexes $[Nb(cp)_2H(CO)]$[1] and $[Nb(cp)_2H\{P(OMe)_3\}]$[6] were prepared according to the literature procedures, $[Fe_2(CO)_9]$ (Aldrich), $[M(CO)_6]$ (M = Mo or W) (Janssen), EtSH (Aldrich) and MeI (Janssen) were used as received and $[M(CO)_5(thf)]$ (M = Mo or W, thf = tetrahydrofuran) were prepared according to literature methods.[11f,17]

Syntheses.—Na(SEt). To a thf solution (80 cm^3) of EtSH (20 cm^3, 270 mmol) was added slowly sodium pellets (6.2 g, 270 mmol). The mixture was stirred at room temperature for 2 d. The sodium salt Na(SEt) was filtered off and the white residue washed with anhydrous diethyl ether (4 × 30 cm^3) and dried *in vacuo* (yield > 90%).

$[Nb(cp)_2(CO)I]$ **1a**. To a thf solution (30 cm^3) of $[Nb(cp)_2H(CO)]$ (0.5 g, 2 mmol) was added methyl iodide (0.12 cm^3, 2 mmol). The mixture was stirred at room temperature for 15 min. The solvent was evaporated and the resulting deep purple solid washed with pentane (2 × 15 cm^3) and dried *in vacuo* yielding 0.75 g of complex **1a** (99%) which is air sensitive (Found: C, 59.80; H, 5.70. Calc. for $C_{11}H_{10}INbO$: C, 61.30; H, 5.80%). ^{1}H NMR (C_6D_6): δ 4.70 (s, cp). IR(thf): ν_{CO} 1935 cm^{-1}.

$[Nb(cp)_2\{P(OMe)_3\}I]$ **1b**. This was prepared by a procedure similar to that applied for complex **1a** from $[Nb(cp)_2H\{P(OMe)_3\}]$ (99% yield) (Found: C, 31.55; H, 3.70. Calc. for $C_{13}H_{19}INbO_3P$: C, 32.95; H, 4.05%). NMR (C_6D_6): ^{1}H, δ 4.75 (s, cp), 3.4 (d, $^{3}J_{HP}$ = 10.5 Hz, 3 OMe); ^{31}P, δ 205.

$[Nb(cp)_2(CO)(SEt)]$ **2a**. To a toluene solution (30 cm^3) of complex **1a** (0.5 g, 1.3 mmol) was added Na(SEt) (0.13 g, 1.5 mmol). The mixture was refluxed for 1 h. The reaction was monitored by IR spectroscopy. After cooling, the mixture was filtered and the solvent removed. The resulting maroon solid was dried under vacuum (yield 0.32 g, 80%) (Found: C, 49.80; H, 4.55. Calc. for $C_{13}H_{15}NbOS$: C, 50.00; H, 4.85%). ^{1}H NMR (CD_3COD_3): δ 5.34 (s, cp), 1.95 (q, $^{3}J_{HH}$ = 7, CH_2) and 1.02 (t, $^{3}J_{HH}$ = 7 Hz, CH_3). IR(thf): ν_{CO} 1920 cm^{-1}.

$[Nb(cp)_2\{P(OMe)_3\}(SEt)]$ **2b**. This was prepared following a procedure similar to that used for complex **2a** in 80% yield from **1b** (Found: C, 43.80; H, 5.70. Calc. for $C_{15}H_{24}NbO_3PS$: C, 44.10; H, 5.90%). NMR (CD_3COD_3): ^{1}H, δ 5.00 (s, cp), 3.64 (d, $^{3}J_{HP}$ = 11, 3 OMe), 1.93 (q, $^{3}J_{HH}$ = 7, CH_2) and 1.04 (t, $^{3}J_{HH}$ = 7 Hz, CH_3); ^{31}P, δ 213.

$[Nb(cp)_2(CO)(\mu\text{-}SEt)\{Mo(CO)_5\}]$ **3a**. To a thf solution (20 cm^3) of complex **2a** (0.2 g, 0.64 mmol) was added at room temperature a 20% excess of $[Mo(CO)_5(thf)]$ in thf (30 cm^3) and the mixture stirred for 1 h. The reaction was monitored by IR spectroscopy. The solvent was removed *in vacuo* and the resulting crude product extracted with toluene (10 cm^3) and chromatographed. The first orange band eluted with toluene gave the complex **3a**. The solvent was evaporated giving 0.20 g of **3a** as an orange solid (yield 57%) (Found: C, 40.45; H, 2.65. Calc. for $C_{18}H_{15}MoNbO_6S$: C, 39.45; H, 2.75%). ^{1}H NMR (CD_3COD_3): δ 5.57 (s, cp), 2.21 (q, $^{3}J_{HH}$ = 7, CH_2) and 1.11 (t, $^{3}J_{HH}$ = 7 Hz, CH_3). IR (thf): ν_{CO} 2064m, 1947s, 1931s and 1890s cm^{-1}.

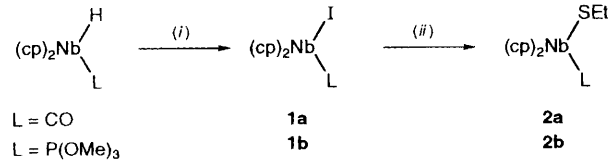
$[Nb(cp)_2(CO)(\mu\text{-}SEt)\{W(CO)_5\}]$ **3b**. This was prepared by a procedure similar to that used for complex **3a** in 60% yield from **2a** and $[W(CO)_5(thf)]$ (Found: C, 33.50; H, 2.30. Calc. for $C_{18}H_{15}NbO_6SW$: C, 34.00; H, 2.40%). ^{1}H NMR (CD_3COD_3): δ 5.59 (s, cp), 2.36 (q, $^{3}J_{HH}$ = 7, CH_2) and 1.09 (t, $^{3}J_{HH}$ = 7 Hz, CH_3). IR (thf): ν_{CO} 2062m, 1946s, 1920s and 1885s cm^{-1}.

$[Nb(cp)_2(CO)(\mu\text{-}SEt)\{Fe(CO)_4\}]$ **3c**. To complex **2a** (0.2 g, 0.64 mmol) in a thf solution (20 cm^3) was added at room temperature $[Fe_2(CO)_9]$ (0.23 g, 0.64 mmol) and the mixture was stirred for 1 h. The reaction was monitored by IR spectroscopy. The solvent was evaporated and the resulting crude product washed with pentane (3 × 15 cm^3) to eliminate $[Fe(CO)_5]$. The solid was then dissolved in toluene (10 cm^3) and chromatographed. The first orange-red band eluted with toluene gave the complex **3c**. The solvent was removed and the red solid dried *in vacuo* (yield 0.18 g, 60%) (Found: C, 41.65; H, 3.20. Calc. for $C_{17}H_{15}FeNbO_5S$: C, 42.55; H, 3.15%). ^{1}H NMR (CD_3COD_3): δ 5.59 (s, cp), 2.35 (q, $^{3}J_{HH}$ = 7 Hz, CH_2) and 1.15 (t, $^{3}J_{HH}$ = 7, CH_3). IR (thf): ν_{CO} 2029m, 1943s, 1923s and 1909s cm^{-1}.

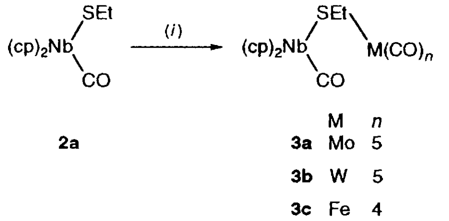
EHMO Calculations.—These calculations[18] were performed on model complexes $[Nb(cp)_2(CO)(PMe_2)]$ and $[Nb(cp)_2(CO)(SMe)]$. The metric parameters for $[Nb(cp)_2(CO)(SMe)]$ were as follows: Cp (geometrical centre of C_5 ring)–Nb 2.08, Nb–S 2.54, Nb–C(CO) 2.04, S–Me 1.8 Å, Cp–Nb–Cp 140°. Those for $[Nb(cp)_2(CO)(PMe_2)]$ and $[Nb(cp)_2(CO)(\mu\text{-}SMe)\{Fe(CO)_4\}]$ were based on the structures of $[Nb(cp)_2(CO)(PPr^{i}Ph)]$[15] and $[Nb(cp)_2(CO)(\mu\text{-}SEt)\{Fe(CO)_4\}]$ **3c**, respectively. These calculations were performed with the EH program contained in the CACAO package.[19] Standard H_{ii} values were used for C and H. Other parameters: O, 2s (H_{ii} −32.30), ξ_1 = 2.275; 2p (−14.80), ξ_1 = 2.275; P, 3s (−18.60), ζ_1 = 1.60; 3p (−14.00), ζ_1 = 1.60; S, 3s (−20.00), ζ_1 = 1.817; 3p (−13.30), ζ_1 = 1.817; Nb, 5s (−10.10), ζ_1 = 1.89; 5p (−6.86), ζ_1 = 1.85; 4d (−12.10 Hz), ζ_1 = 4.08, ζ_2 = 1.64, C_1 = 0.6401 and C_2 = 0.5516.

X-Ray Analysis of Complex **3c**.—Recrystallization of complex **3c** from CH_2Cl_2 solution gave small crystals suitable for diffraction measurements. An irregularly shaped red crystal having approximate dimensions 0.15 × 0.10 × 0.10 mm was used for unit-cell determination and data collection, carried out at 296(1) K on an Enraf-Nonius CAD4 diffractometer with Mo-Kα radiation (λ = 0.710 73 Å). The pertinent crystallographic data are given in Table 1. All calculations were carried out by use of the MOLEN package[20] with neutral-atom scattering factors. Intensities were corrected for Lorentz and polarization effects. Systematic extinctions indicated either the centrosymmetric *Pnma* or the non-centrosymmetric *Pna*2_1 orthorhombic space groups, thus the resolution of the structure was attempted in both. An analysis of three dimensional Patterson and Fourier-difference maps strongly favoured the *Pnma* group. All non-hydrogen atoms could be easily located, while several difficulties were encountered for location of one carbonyl ligand bound to the iron atom and of some carbon atoms of cyclopentadienyl rings with *Pna*2_1. Moreover, some unusual values of geometrical parameters (bond distances and angles) were observed with the latter. The *Pnma* space group was thus adopted. Some atoms were found on the mirror plane: both metals, carbonyl bound to the niobium, two carbonyls from $Fe(CO)_4$ and the terminal carbon atom of SEt. The bridging sulfur atom and methylene carbon of this last ligand are disordered over the mirror plane. This observation indicated a non-centrosymmetric group. However, it will be shown in the discussion of the EHMO results that an inversion of conformation at sulfur requires very little energy. Thus, a disorder of a centrosymmetric group may easily be explained. After isotropic refinement of the model, the hydrogen atoms were placed in calculated positions, and an empirical absorption correction (DIFABS[21]) was applied. All non-hydrogen atoms were further refined with anisotropic thermal parameters. The hydrogen atoms were included in a riding model with B_{iso} fixed at 1.3 B_{eq} for the carbon atoms to which they are bonded. Full-matrix least-squares refinement of 1153 unique reflections with $I > 2.5\sigma(I)$ converged at $R = 0.068$ (maximum shift/error = 0.03). The coordinates of non-hydrogen atoms are given in Table 2. Atomic scattering factors and anomalous dispersion coefficients were taken from the usual sources.[22]

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.



Scheme 1 (*i*) MeI; (*ii*) Na(SEt)



Scheme 2 (*i*) [Fe$_2$(CO)$_9$] or [M(CO)$_5$(thf)] (M = Mo or W)

Results and Discussion

Chemistry.—The complexes [Nb(cp)$_2$L(I)][L = CO **1a** or P(OMe)$_3$ **1b**] are easily formed by the reactions of [Nb(cp)$_2$H(L)] hydrides with MeI (Scheme 1) in quantitative yields. Stirring of complexes **1** with Na(SEt) in refluxing toluene gives after work-up the thiolato derivatives **2**. The new complexes **1** and **2** were characterized by ^{1}H and ^{31}P NMR and IR spectroscopies (Experimental section).

The chemical shifts and ν_{CO} frequencies of iodo complexes **1** are close to the values reported for [Nb(cp)$_2$L(X)](X = Cl or Br).[2,3] The ^{1}H NMR resonance of the cyclopentadienyl protons in **2a** (L = CO, δ 5.34) is at lower field than that for **2b** [L = P(OMe)$_3$, δ 5.00]. This is consistent with the better π-acceptor property of CO than of P(OMe)$_3$ and indicates that lower electron density is retained on the (cp)$_2$Nb (Nb^{III}, d^2) unit in complex **2a** than in **2b**. Similar behaviour has been observed for terminal phosphido complexes [Nb(cp)$_2$L(PPh$_2$)] [L = CO or P(OMe)$_3$].[6] The cyclopentadienyl protons resonate at lower fields for thiolato compounds than for phosphido ones {*e.g.* [Nb(cp)$_2$(CO)(PMe)$_2$] δ(CD$_3$COCD$_3$) 5.03}.[5] This may suggest that the PR$_2$ groups behave as better electron donors than do the SR ligands.

The monobridged heterobimetallic complexes **3** were synthesized by the reactions of [Nb(cp)$_2$(CO)(SEt)] **2a** with [Fe$_2$(CO)$_9$] and [M(CO)$_5$(thf)] (Scheme 2). There are some noteworthy differences in chemical behaviour between terminal thiolato and terminal phosphido complexes. The analogous reactions with phosphido complexes [Nb(cp)$_2$(CO)(PR$_2$)] (R = Me or Ph) produced both mono- (μ-PR$_2$) and di-bridged (μ-PR$_2$, μ-CO) molecules.[5,6] In the case of thiolato complex **2a** no dibridged compound (μ-SEt, μ-CO) was detected upon heating or UV irradiation. With [Nb(cp)$_2${P(OMe)$_3$}(SEt)] **2b** no formation of a μ-SEt bimetallic complex was observed in the presence of [Fe$_2$(CO)$_9$] or [M(CO)$_5$(thf)] while the related phosphido compound [Nb(cp)$_2${P(OMe)$_3$}(PPh$_2$)] binds M(CO)$_5$ fragments to form the corresponding monophosphido-bridged molecules.[6]

In the bimetallic systems **3** the ^{1}H resonances of the cp ligands (δ ≈5.58) are shifted downfield with respect to the parent thiolate **2a** (δ 5.34). Similar observations have been reported for ^{1}H chemical shifts of the niobophosphine [Nb(cp)$_2$(CO)(PMe$_2$)] and the corresponding monobridged complexes [Nb(cp)$_2$(CO)(μ-PMe$_2$){M′(CO)$_n$}]^5. For complexes **3** the cyclopentadienyl protons are also shifted downfield with respect to the related phosphido-bridged bimetallics [Nb(cp)$_2$(CO)(μ-PMe$_2$){M′(CO)$_n$}] (δ ≈5.4).[5] A similar trend has been observed for monocyclopentadienyl bimetallics, *e.g.* δ 5.32 (CDCl$_3$) for [W(cp)(CO)$_3$(μ-PPh$_2$)-{Mo(CO)$_5$}][23] and δ 5.68 (CDCl$_3$) for [W(cp)(CO)$_3$(μ-SMe)-{W(CO)$_5$}].[12a]

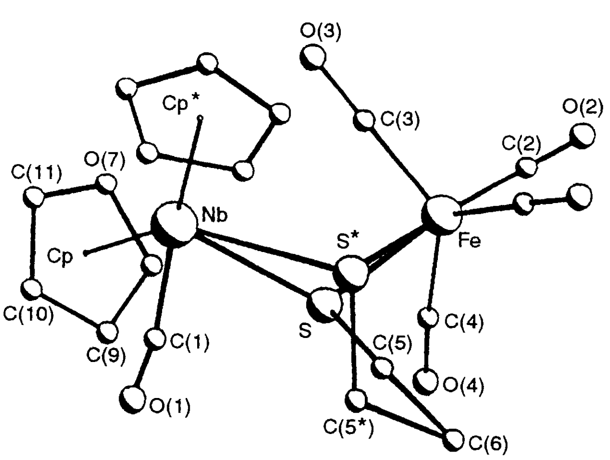


Fig. 1 Molecular structure of [Nb(cp)$_2$(CO)(μ-SEt){Fe(CO)$_4$}] **3c**

The IR data for the dinuclear complexes **3** exhibit the typical patterns of Fe(CO)$_4$ (**3c**) and M(CO)$_5$ (Mo **3a**, W **3b**) fragments with an additional ν_{CO} band near 1925 cm^{-1} due to the presence of a carbonyl ligand bound to the niobium atom. The ν_{CO} frequencies of the Fe(CO)$_4$ fragment are close to those reported for related phosphido-bridged complexes, *e.g.* for [Nb(cp)$_2$-(CO)(μ-PMe$_2$){Fe(CO)$_4$}] ν_{CO} 2020, 1943, 1929 and 1901 cm^{-1}.[5] They show, however, a red shift (Δν 20 cm^{-1}) with respect to the values observed for the mononuclear complexes [Fe(CO)$_4$L] (*e.g.* L = PBu$_3$, ν_{CO} 2047, 1974 and 1935 cm^{-1}).[24] The same trend is valid for **3a** and **3b** by comparison with [M(CO)$_5$L] (M = Mo or W) systems.[25] This confirms that the metallophosphines [Nb(cp)$_2$(CO)(PR$_2$)] as well as the thiolate [Nb(cp)$_2$(CO)(SEt)] are electron rich and exhibit a similar electronic behaviour upon co-ordination to metal carbonyls.

Molecular Structure of [Nb(cp)$_2$(CO)(μ-SEt){Fe(CO)$_4$}] **3c**.—The molecular structure of complex **3** is shown in Fig. 1. Selected bond lengths and angles are given in Table 3. The Nb shows the usual distorted-tetrahedral geometry characteristic of bent metallocenes, whereas the co-ordination polyhedron of iron is a distorted trigonal bipyramid.

The Nb···Fe separation of 4.306(2) Å is clearly non-interacting. The Nb–S distance [2.590(5) Å)] is longer than in the mononuclear niobium(III) complex [Nb(cp)$_2$(CO)(SH)] [2.539(4) Å][7] and in mononuclear complexes of Nb^{IV} and Nb^{V} with two terminal SR ligands [Nb(cp)$_2$(SR)$_2$] (R = C$_6$H$_4$X-*p*, X = H, Me, OMe or Cl) where it falls in the range 2.41–2.52 Å.[26] This distance is also longer than in [Nb(cp)$_2$-(μ-SPh)$_2${Mo(CO)$_4$}][26a] and [{Nb(cp)$_2$(μ-SMe)$_2$}$_2$Ni]BF$_4$[26c] heterobimetallics (2.47–2.50 Å), but it is close to the values reported for the Nb–Nb bonded homonuclear dimers with two SR (R = H or Me) bridges [2.55(1)–2.58(1) Å].[27] The presence of the long Nb–S bond in **3c** may be due to the repulsions between (*i*) the niobium(III) lone pair and that retained on the sulfur atom and (*ii*) the (cp)$_2$Nb(CO) and Fe(CO)$_4$ fragments. The Fe–S bond length of 2.366(5) Å falls in the upper range of values observed in Fe–S–M linkages with μ-alkanethiolates.[28]

The S–Nb–C(CO) angle [88.5(5)°] is smaller than that found in [Nb(cp)$_2$(CO)(SH)] [92.3(5)°][7] but corresponds very well to the P–Nb–C(CO) angles observed in the monobridged [Nb(cp)$_2$L(μ-PPh$_2$){Cr(CO)$_5$}] [L = CO or P(OMe)$_3$] complexes.[6] It is significantly larger than the S–M–S angles (72–85°) observed in dithiolato metallocenes (metal d^2), but falls in the range of values suggested for metal d^1 dithiolates.[26b] This

Table 1 Crystallographic data for $[Nb(cp)_2(CO)(\mu\text{-}SEt)\{Fe(CO)_4\}]$ **3c**

Molecular formula	$C_{17}H_{15}FeNbO_5S$
M	480.12
Crystal system	Orthorhombic
Space group	*Pnma* (no. 62)
a/Å	18.724(6)
b/Å	11.246(6)
c/Å	8.738(6)
U/Å^3	1839.9
Z	4
D_c/g cm^{-3}	1.733
μ/cm^{-1}	15.159
$F(000)$	960
Scan type	ω–2θ
Scan speed/° min^{-1}	4.1–16.5
Scan width/°	$1.0 + 0.34 \tan\theta$
θ Range/°	2–25
No. of reflections measured	4044
Linear decay (%)	−21.7, corrected
Minimum, maximum absorption correction	0.3773, 1.7762
No. of unique observed data $[I > 2.5\sigma(I)]$, N_o	1153
No. of variables, N_v	136
$R(F)$[a]	0.068
$R'(F)$[b]	0.070
$w = 1/\sigma(F_o)^2 = [\sigma(I)^2 + (pF_o^2)^2]^{-\frac{1}{2}}, p$	0.05
Goodness of fit	0.763
ρ_{max}/e Å^{-3}	1.36 (near Nb)

[a] $R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R'(F) = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(F_o)^2]^{\frac{1}{2}}$.

Table 2 Atomic coordinates of the non-hydrogen atoms of complex **3c**

Atom	*x*	*y*	*z*
Nb	0.349 00(7)	0.75	0.638 8(2)
Fe	0.129 2(1)	0.75	0.493 8(2)
S	0.214 6(3)	0.789 7(4)	0.686 7(6)
Cp	0.374 7	0.920 8	0.577 0
O(1)	0.382 2(9)	0.75	0.997(2)
O(2)	0.014 7(7)	0.75	0.271(2)
O(3)	0.236 7(7)	0.75	0.246(1)
O(4)	0.079 2(6)	0.979 7(8)	0.609(1)
C(1)	0.364 1(9)	0.75	0.871(2)
C(2)	0.060 2(9)	0.75	0.359(2)
C(3)	0.194 0(8)	0.75	0.344(2)
C(4)	0.101 2(8)	0.893(1)	0.567(1)
C(5)	0.188(1)	0.711(1)	0.855(2)
C(6)	0.118 3(7)	0.75	0.918(2)
C(7)	0.364 1(9)	0.901(1)	0.449(2)
C(8)	0.315 5(8)	0.942(1)	0.550(2)
C(9)	0.348 2(8)	0.953(1)	0.691(2)
C(10)	0.418 8(8)	0.923(1)	0.671(2)
C(11)	0.426 8(8)	0.888(1)	0.524(2)

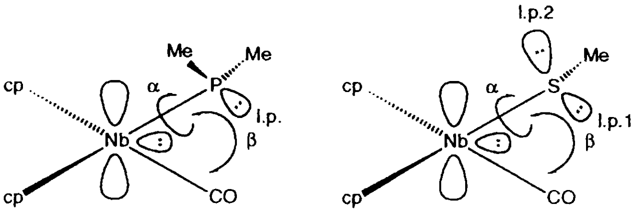
Cp is the centroid of atoms C(7)–C(11).

Table 3 Selected interatomic distances (Å) and angles (°) for complex **3c**

Nb · · · Fe	4.306(2)	Fe–C(3)	1.78(2)
Nb–S	2.590(5)	Fe–C(4)	1.81(1)
Nb–C(1)	2.04(2)	S–C(5)	1.79(2)
Fe–S	2.366(5)	C(1)–O(1)	1.16(2)
Fe–C(2)	1.75(2)	Nb–Cp	2.05
Nb–S–Fe	120.6(2)	S–Fe–C(3)	93.6(5)
Nb–S–C(5)	108.4(7)	S–Fe–C(4)	96.5(4)
S–Nb–C(1)	88.5(5)	cp–Nb–cp*	138.8
S–Fe–C(2)	168.4(2)		

indicates that the strong Nb to CO π back bonding decreases the electron density on the $(cp)_2Nb$ unit (its $1a_1$ frontier orbital), thus allowing the S–Nb–C(CO) angle to open. It is consistent with the *endo* structure adopted by the ethyl group in **3c**. On the other hand, the Nb–S–Fe angle [120.6(2)°] is smaller than the M–P–M′ angles in the monophosphido-bridged complexes cited above [125.94(8) and 129.11(5)°]. The angle found here is close to W–S–W [119.7(1)°] for $[(OC)_3(cp)W(\mu\text{-}SMe)W(CO)_5]$ but much smaller than that observed in $[(OC)(F_3CC_2CF_3)(cp)W(\mu\text{-}SMe)W(CO)_5]$ [131.5(1)°].[12a] This means that the values of the M–X–M′ (X = P or S) angles in the phosphido and thiolato monobridged bimetallics are mostly governed by steric repulsions between the organometallic fragments.

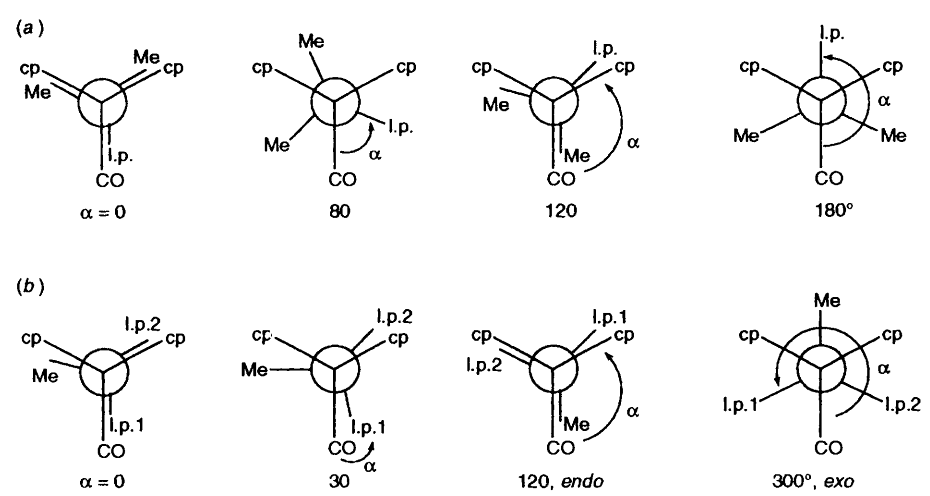
The dihedral angle C(CO)NbS/NbSFe is equal to 19.3°. Other geometric parameters are normal.



Scheme 3 l.p. = Lone pair

Electronic Structures.—According to the bonding model of d^2 bent metallocenes of the type $[Nb(cp)_2(CO)X]$,[29] the metal lone pair occupies the molecular orbital ($1a_1$ in C_{2v} symmetry) located in the P (or S), Nb, CO plane. We have performed conformational studies on two models $[Nb(cp)_2(CO)X]$ with X = PMe_2 or SMe by varying two angular parameters α and β (Scheme 3). Angle α = 0° corresponds to the conformation in which the metal lone pair and that of phosphorus are in the P,Nb,CO plane for the phosphido complex, and the metal lone pair and one of the two sulfur lone pairs in the S, Nb, CO plane for the thiolato compound. The angle α has been allowed to vary from 0 to 300° spanning all possible conformations, and β from 75 (PMe_2) or 69 (SMe) to 93°. The acute β angles, not observed in real structures, were used in order to estimate the steric effects. The Newman-type projections for $[Nb(cp)_2(CO)(PMe_2)]$ and for $[Nb(cp)_2(CO)(SMe)]$ complexes are presented in Scheme 4(*a*) (PMe_2) and (*b*) (SMe), respectively.

Representative curves of the variation in total molecular energy (E_{tot}) and of the difference (ΔE) between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) as a function of α for β = 87° for $[Nb(cp)_2(CO)(PMe_2)]$ and $[Nb(cp)_2(CO)(SMe)]$ are shown in Fig. 2. The value β = 87° corresponds to the P–Nb–CO angles generally observed in niobium(III) metallophosphines, and to the S–Nb–CO angle found in the structure of complex **3c**. Curves corresponding to other β values may be obtained from the authors. The shapes of the curves obtained for the niobophosphine $[Nb(cp)_2(CO)(PMe_2)]$ are very close to those reported for the complex $[Mo(cp)_2H(PH_2)]$[11f] which suggests that the 'transition-metal *gauche* effect' operates in a similar manner in $Mo^{IV}H$ (d^2) and in $Nb^{III}(CO)$ (d^2) metallocenes. The total-energy curve for $[Nb(cp)_2(CO)(PMe_2)]$ shows two minima. That at α = 80° (and 280° by symmetry) is somewhat deeper than the second one at α = 180°. This may be attributed to steric constraints induced by the presence of the methyl groups. It is expected that bulkier phenyl groups (X = PPh_2) would enlarge this difference by increasing the total energy at α = 180°, thus favouring a conformation with α close to 80°. This hypothesis is supported by the structure of $[Nb(cp)_2(CO)(PPr^iPh)]$ in which α ≈ 74°.[15] The ΔE curve for $[Nb(cp)_2(CO)(PMe_2)]$ exhibits a minimum at α = 180° corresponding to the conformation in which both lone pairs are placed in the same plane. Thus, it seems reasonable to assume that the ΔE *vs.* α function represents mostly the electronic



Scheme 4 l.p. = Lone pair

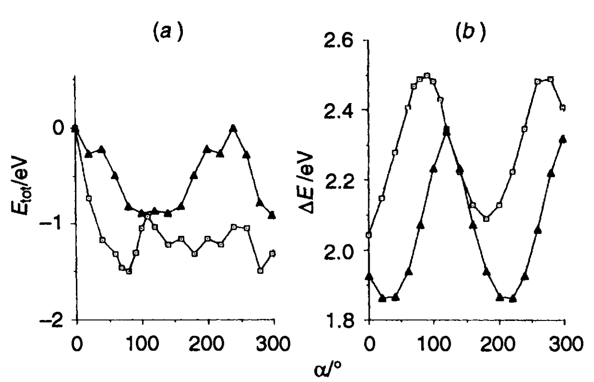


Fig. 2 Variations of the relative total energies (E_{tot}) (*a*) and of ΔE (HOMO − LUMO) (*b*) as a function of α in [Nb(cp)$_2$(CO)X] for β = 87°, X = PMe$_2$(□) or SMe (▲)

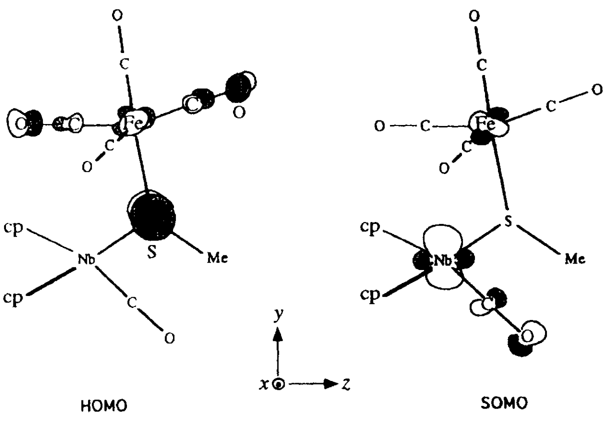


Fig. 3 Shapes of the highest occupied molecular orbitals for [Nb(cp)$_2$(CO)(μ-SMe){Fe(CO)$_4$}]

effects, while E_{tot} *vs.* α involves both electronic and steric effects.

The ΔE *vs.* α curve for [Nb(cp)$_2$(CO)(SMe)] exhibits a similar shape to that observed for the metallophosphine, but shifted by 30°. The minimum at 30° (and 210° by symmetry) corresponds to the repulsions between the sulfur lone pairs and the two lobes of the 1a$_1$ metallocene orbital occupied by its lone pair. This is confirmed by a smaller value of the minimum ΔE for the thiolato complex than for the metallophosphine where only one lone pair of phosphorus may interact with one lobe of the 1a$_1$ metal orbital. The stable conformations suggested by the maxima in ΔE are found at α = 120 (*endo*) and 300° (*exo*). They agree with the minima found in the E_{tot} *vs.* α curve. It is interesting that for β = 87° the minimum in E_{tot} observed for the *endo* conformation is almost flat from α = 100 to 140° which means that deviations of α by ± 20° from the stable *endo* conformation may easily occur. This is in good agreement with the dihedral angle C(CO)NbS/NbSFe observed in **3c** (19.3°). The disordered positions of the chiral sulfur atom in 3c correspond to the *S* and *R* optical isomers, both occurring alternately from one unit cell to another. Thus, the EHMO calculations and the X-ray results indicate a low energy for inversion at the sulfur atom. Low inversion energies have previously been observed in other terminal and bridged thiolato complexes.[12b,26b,30]

The different chemical behaviour of the phosphido and thiolato complexes, consisting of the formation or non-formation of dibridged species (μ-X, μ-CO), deserves comment. Apparently, this difference does not result from hindered rotation of the M(CO)$_n$ fragment around the Nb–S bond, because both conformations, α = 75 (monobridged μ-PPh$_2$)[6,11c,d] and 180° (monobridged μ-PMe$_2$),[5,11e] convert into dibridged Nb(μ-PR$_2$, μ-CO)M structures. However, even if the Nb–S bond is long in the structure of **3c**, it remains shorter by more than 0.1 Å than the Nb–P distances observed in monophosphido-bridged compounds. Thus, orientation of the M(CO)$_n$ fragment to allow the formation of a second bridge cannot be attained. Steric effects are probably responsible for the non-formation of μ-SEt bimetallics in the case of the [Nb(cp)$_2${(P(OMe)$_3$}(SEt)] complex. Electronic effects may also play an important role. The shapes of the HOMO and singly occupied molecular orbital (SOMO) obtained from EHMO calculations for the model [Nb(cp)$_2$(CO)(μ-SMe)-{Fe(CO)$_4$}] are shown in Fig. 3. These molecular orbitals are perpendicular. The HOMO, which comprises at least 50% of the sulfur lone pair, and the SOMO mainly comprising the 1a$_1$ (cp)$_2$Nb fragment, are well separated molecular orbitals representing two lone pairs: one on the ligand and the other on the niobium atom. The conditions necessary for operation of the 'transition-metal *gauche* effect' are thus respected. We conclude that both the steric and electronic effects may be responsible for the chemical differences observed between the phosphido and thiolato complexes.

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