Synthesis and Structural Characterisation of New Isocyanate and Imido Niobocene Complexes. Crystal Structures of [{Nb(η-$C_5H_4SiMe_3$)$_2$Cl}$_2$] and [Nb(η-$C_5H_4SiMe_3$)$_2$(=NPh)Cl]†

Antonio Antiñolo,[a] Pedro Espinosa,[b] Mariano Fajardo,[b] Pilar Gómez-Sal,[d] Carmen López-Mardomingo,[c] Avelino Martin-Alonso[d] and Antonio Otero*,[a]
[a] *Departamento de Química Inorgánica, Orgánica y Bioquímica, Facultad de Químicas, Campus Universitario, Universidad de Castilla-La Mancha, 13071 – Ciudad Real, Spain*
[b] *Departamento de Química Inorgánica, Campus Universitario, Universidad de Alcalá, 28871-Alcalá de Henares, Spain*
[c] *Departamento de Química Orgánica, Campus Universitario, Universidad de Alcalá, 28871-Alcalá de Henares, Spain*
[d] *Unidad de Rayos X, Campus Universitario, Universidad de Alcalá, 28871-Alcalá de Henares, Spain*

The isocyanate complexes [Nb(η-$C_5H_4SiMe_3$)$_2$(RNCO)Cl] (R = Ph **2**, Bu^t **3**, Pr^n **4**, Pr^i **5**) have been prepared from the reaction of [Nb(η-$C_5H_4SiMe_3$)$_2$Cl] **1** with the appropriate ligands. Treatment of **1** with the corresponding amines NH_2R afforded the imido complexes [Nb(η-$C_5H_4SiMe_3$)$_2$(=NR)Cl] (R = Ph **6**, Bu^t **7**, Pr^n **8** or Pr^i **9**) which can also be prepared by thermal treatment of the corresponding isocyanate complexes **2**–**5**. All complexes have been characterised in solution by both ^{1}H and ^{13}C NMR spectroscopy. Complex **1** crystallises in the monoclinic space group $P2_1/c$ showing two crystallographic independent molecules with $Z = 8$, $a = 12.968(4)$, $b = 23.988(7)$, $c = 25.546(7)$ Å and $\beta = 103.22(3)°$. It has a binuclear structure with two almost symmetrical chloride bridges, giving a closed-shell, 18-electron configuration. Complex **6** crystallises in the monoclinic space group $P2_1/n$ with $Z = 4$, $a = 7.343(2)$, $b = 16.880(3)$, $c = 20.227(4)$ Å and $\beta = 96.41(2)°$. The structure shows a value of 165.1(2)° for the Nb–N–C angle and an Nb–N bond distance of 1.792(2) Å, intermediate between that expected for double and triple bonds.

Metal-promoted activations of heterocumulenes are of increasing interest since they may provide a model for metal-induced transformations on carbon dioxide.[1] Although numerous studies on the reactivity of isocyanates toward several metal centres have been described,[2] few examples of complexes containing the metal isocyanate moiety are known[3] due in part to the high reactivity exhibited by the isocyanates. On the other hand, the chemistry of complexes containing multiply bonded ligands, such as the imide group, has spiralled in recent years.[4] Although the imide ligand has been employed as an ancillary group to support high-oxidation-state metal centres, an increasing number of complexes having reactive imide ligands have been shown to participate in C–H bond activation[5] and cycloaddition reactions.[6] It is noteworthy that early transition metal–imido complexes are widely represented and a great number of established imido functional groups of d^0 niobium and tantalum are known.[7] However, despite the fact that the chemistry of monocyclopentadienyl imido complexes of these metals is well represented[8] few examples of imido bent metallocenes have been described.[9] We previously reported that the carbenoid-like complex [Nb(η-$C_5H_4SiMe_3$)$_2$Cl] is a versatile starting material for the activation of a variety of cumulenes, such as ketenes, ketenimines, *etc.*[10] We have recently become interested in studying compounds containing isocyanate and organoimide ligands. In this article we report our efforts to prepare isocyanate niobocene derivatives, [Nb(η-$C_5H_4SiMe_3$)$_2$(RNCO)Cl] (R = Ph, Bu^t, Pr^n or Pr^i), and the development of new synthetic routes to imido niobocene complexes, [Nb(η-$C_5H_4SiMe_3$)$_2$(=NR)Cl], as well as the crystal structure determinations for [Nb(η-$C_5H_4SiMe_3$)$_2$Cl] and [Nb(η-C_5-H_4SiMe_3)$_2$(=NPh)Cl], the first of which exhibits a symmetrical double chloride bridge and the second a niobium–imido bond.

Results and Discussion

Several years ago we described[9a] the synthesis of the monochloro niobocene complex [Nb(η-$C_5H_4SiMe_3$)$_2$Cl] **1** by reduction of [Nb(η-$C_5H_4SiMe_3$)$_2Cl_2$] with 1 equivalent of Na–Hg. The complex was isolated from a hexane solution as a very air-sensitive brown microcrystalline solid. It was characterised by ^{1}H and ^{13}C NMR spectroscopy and its spectra in C_6D_6 indicated the presence of two equivalent cyclopentadienyl rings. In order to achieve a closed-shell 18-electron configuration, a binuclear structure with two symmetrical chloride bridges was proposed, although alternative structures such as a stable monomer, a symmetrical trimer or even a polymeric structure could not be definitively excluded. In related complexes such as [Ta(η-C_5Me_5)$_2$Cl] an unsymmetrical dimeric structure has been proposed while [V(η-C_5Me_5)$_2$Cl] and [Ti(η-C_5Me_5)$_2$Cl] have both been reported to be stable monomers.[9e,11] In order to establish the definitive structure for our complex its crystal structure was determined. Fig. 1 shows the structure of **1**, Table 1 the selected bond lengths and angles, and Table 2 the atomic coordinates for all non-hydrogen atoms.

Complex **1** exhibits a binuclear structure as proposed, in a typical bent metallocene arrangement exhibiting two bridging chlorides located in the plane which bisects the dihedral angle formed by the cyclopentadienyl rings. Interestingly, the

---

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

Non-SI unit employed: eV ≈ 1.60×10^{-19} J.

Table 1 Selected bond lengths (Å) and angles (°) for complex **1**

Molecule 1				Molecule 2			
Nb(1)–Cl(2)	2.580(2)	Nb(1)–Cl(1)	2.587(2)	Nb(3)–Cl(3)	2.569(3)	Nb(3)–Cl(4)	2.575(3)
Nb(2)–Cl(2)	2.573(2)	Nb(2)–Cl(1)	2.577(2)	Nb(4)–Cl(3)	2.582(3)	Nb(4)–Cl(4)	2.587(2)
Si(1)–C(18)	1.837(12)	Si(1)–C(16)	1.847(13)	Si(5)–C(56)	1.848(11)	Si(5)–C(58)	1.837(12)
Si(1)–C(17)	1.852(12)	Si(1)–C(11)	1.864(9)	Si(5)–C(51)	1.849(9)	Si(5)–C(57)	1.859(13)
Si(2)–C(28)	1.847(11)	Si(2)–C(27)	1.848(12)	Si(6)–C(66)	1.833(14)	Si(6)–C(67)	1.855(13)
Si(2)–C(26)	1.857(10)	Si(2)–C(21)	1.869(9)	Si(6)–C(61)	1.861(10)	Si(6)–C(68)	1.863(13)
Si(3)–C(37)	1.79(2)	Si(3)–C(36)	1.82(2)	Si(7)–C(77)	1.82(2)	Si(7)–C(71)	1.843(10)
Si(3)–C(38)	1.85(2)	Si(3)–C(31)	1.855(9)	Si(7)–C(76)	1.857(11)	Si(7)–C(78)	1.862(14)
Si(4)–C(47)	1.840(13)	Si(4)–C(41)	1.846(9)	Si(8)–C(86)	1.76(2)	Si(8)–C(87)	1.78(2)
Si(4)–C(46)	1.845(12)	Si(4)–C(48)	1.846(12)	Si(8)–C(81)	1.854(9)	Si(8)–C(88)	1.86(2)
Cl(2)–Nb(1)–Cl(1)	74.8(1)	Cl(2)–Nb(2)–Cl(1)	75.1(1)	Cl(3)–Nb(3)–Cl(4)	74.9(1)	Cl(3)–Nb(4)–Cl(4)	74.5(1)
Nb(2)–Cl(1)–Nb(1)	104.9(1)	Nb(2)–Cl(2)–Nb(1)	105.2(1)	Nb(3)–Cl(3)–Nb(4)	105.5(1)	Nb(3)–Cl(4)–Nb(4)	105.2(1)
C(18)–Si(1)–C(16)	109.0(6)	C(18)–Si(1)–C(17)	111.8(6)	C(56)–Si(5)–C(58)	109.0(6)	C(56)–Si(5)–C(51)	110.4(5)
C(16)–Si(1)–C(17)	105.9(6)	C(18)–Si(1)–C(11)	107.9(5)	C(58)–Si(5)–C(51)	111.2(5)	C(56)–Si(5)–C(57)	107.4(6)
C(16)–Si(1)–C(11)	114.1(5)	C(17)–Si(1)–C(11)	108.3(5)	C(58)–Si(5)–C(57)	110.8(6)	C(51)–Si(5)–C(57)	108.0(5)
C(28)–Si(2)–C(27)	107.2(6)	C(28)–Si(2)–C(26)	109.5(5)	C(66)–Si(6)–C(67)	109.8(7)	C(66)–Si(6)–C(61)	107.5(6)
C(27)–Si(2)–C(26)	110.5(5)	C(28)–Si(2)–C(21)	112.4(5)	C(67)–Si(6)–C(61)	111.7(5)	C(66)–Si(6)–C(68)	107.8(7)
C(27)–Si(2)–C(21)	108.2(5)	C(26)–Si(2)–C(21)	109.0(5)	C(67)–Si(6)–C(68)	110.3(6)	C(61)–Si(6)–C(68)	109.7(6)
C(37)–Si(3)–C(36)	111.1(8)	C(37)–Si(3)–C(38)	110.4(7)	C(77)–Si(7)–C(71)	113.5(6)	C(77)–Si(7)–C(76)	109.5(7)
C(36)–Si(3)–C(38)	103.4(8)	C(37)–Si(3)–C(31)	110.6(6)	C(71)–Si(7)–C(76)	109.8(5)	C(77)–Si(7)–C(78)	109.0(7)
C(36)–Si(3)–C(31)	110.9(7)	C(38)–Si(3)–C(31)	110.3(6)	C(71)–Si(7)–C(78)	105.8(6)	C(76)–Si(7)–C(78)	109.0(6)
C(47)–Si(4)–C(41)	108.1(5)	C(47)–Si(4)–C(46)	107.6(6)	C(86)–Si(8)–C(87)	118.5(9)	C(86)–Si(8)–C(81)	114.7(7)
C(41)–Si(4)–C(46)	110.3(6)	C(47)–Si(4)–C(48)	109.1(6)	C(87)–Si(8)–C(81)	109.8(7)	C(86)–Si(8)–C(88)	104.1(9)
C(41)–Si(4)–C(48)	110.6(5)	C(46)–Si(4)–C(48)	111.0(6)	C(87)–Si(8)–C(88)	101.5(9)	C(81)–Si(8)–C(88)	106.5(8)

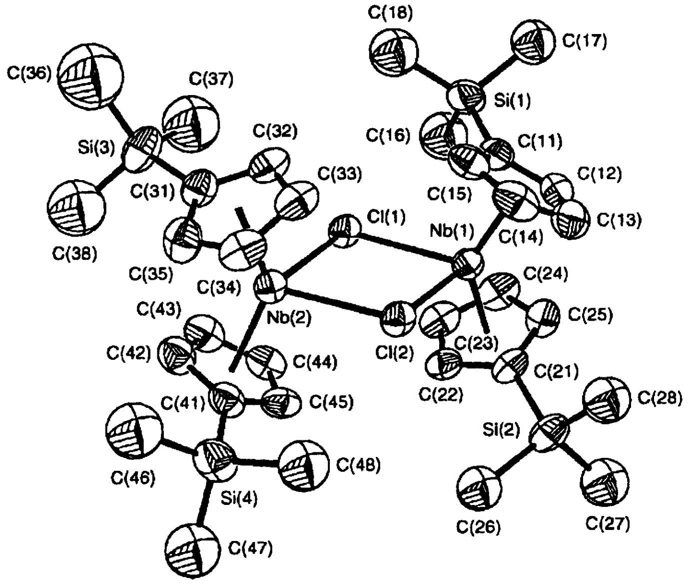


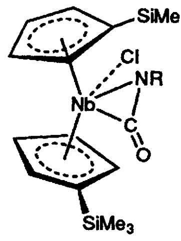
Fig. 1 An ORTEP[12] view of the complex $[\{Nb(\eta\text{-}C_5H_4SiMe_3)_2Cl\}_2]$ **1**

chlorides are symmetrically situated in the $(C_5H_4)_2Nb$ wedges and the bond lengths in Nb–Cl–Nb are practically equal. An unsymmetrical dimeric structure has previously been reported[13] for $[\{Y(\eta\text{-}C_5Me_5)Cl\}_2]$ with one terminal and one bridging chloride, but as far as we are aware the structure of **1** represents the first example of a dimeric structure with a symmetrical bridging disposition. Once the structure of **1** was established, we undertook a study of its reactivity toward organic isocyanates.

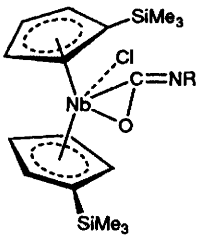
Treatment of a hexane solution of **1** with several of these molecules leads to the formation of precipitates which correspond to $[Nb(\eta\text{-}C_5H_4SiMe_3)_2(RNCO)Cl]$ species **2**–**5** in accordance with equation (1). Complex **2** was prepared

$$[\{Nb(\eta\text{-}C_5H_4SiMe_3)_2Cl\}_2] + 2RNCO \longrightarrow [Nb(\eta\text{-}C_5H_4SiMe_3)_2(RNCO)Cl] \quad (1)$$

$$R = Ph\ \mathbf{2},\ Bu^t\ \mathbf{3},\ Pr^n\ \mathbf{4}\ \text{or}\ Pr^i\ \mathbf{5}$$



a



b

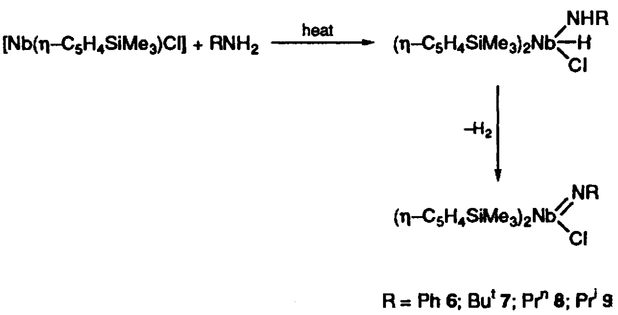
previously[9a] using this method, which constitutes an excellent way of co-ordinating a heterocumulene. Complexes **2**–**5** represent the first examples of isocyanate complexes of early transition metals. Floriani and co-workers[2d] reported the reactivity of $[Ti(\eta\text{-}C_5H_5)_2(CO)_2]$ with PhNCO, but in all cases species containing the ureylene ligand –NRC(O)NR′– derived from isocyanate were isolated (R,R′ = alkyl or aryl).

The IR spectra for complexes **2**–**5** display a strong band at *ca.* 1750 cm^{-1} (see Experimental section) which can be assigned to either the ν(C=O) or ν(N=C) stretching vibration depending on whether co-ordination of RNCO occurs through the C=N or the C=O. The ^{13}C NMR spectra show a resonance at *ca.* δ 180.0 (see Experimental section) which could be due to C=N or C=O. We have no additional data to establish whether the structure of our complexes is either as in *a* or *b*, although to our knowledge there are no examples of an η-C,O-bonded organic isocyanate.

Complex **1** is also a suitable starting material for a variety of imido niobocene derivatives. The reaction with amines RNH_2 affords $[Nb(\eta\text{-}C_5H_4SiMe_3)_2(=NR)Cl]$ and dihydrogen, in accordance with a sequence involving initial oxidative addition of the amine, giving rise presumably to an amido intermediate which on subsequent thermolytic expulsion of H_2 affords the imido derivatives (Scheme 1). The dihydrogen evolved was collected and identified, but attempts to identify the supposed amido intermediate failed (monitored by NMR experiments), due probably to the rapid elimination of H_2 under the experimental conditions (see Experimental section).

Table 2 Atomic coordinates (× 10^4) for complex **1**

Atom	x	y	z	Atom	x	y	z
Molecule 1				Molecule 2			
Nb(1)	8 242(1)	8 596(1)	1 827(1)	Nb(3)	5 133(1)	2 485(1)	839(1)
Nb(2)	8 598(1)	6 901(1)	1 810(1)	Nb(4)	8 033(1)	2 601(1)	463(1)
Cl(1)	9 561(2)	7 802(1)	2 193(1)	Cl(3)	6 216(2)	3 089(1)	330(1)
Cl(2)	7 311(2)	7 693(1)	1 421(1)	Cl(4)	6 948(2)	2 000(1)	983(1)
Si(1)	11 000(2)	9 130(1)	1 871(1)	Si(5)	3 653(2)	3 827(1)	926(1)
Si(2)	5 327(2)	8 780(1)	1 807(1)	Si(6)	4 191(3)	1 008(1)	1 012(1)
Si(3)	11 369(2)	6 280(1)	1 996(1)	Si(7)	8 833(3)	4 121(1)	397(1)
Si(4)	6 110(2)	5 996(1)	1 622(1)	Si(8)	9 173(3)	1 178(2)	316(1)
C(11)	9 587(7)	9 031(4)	1 517(4)	C(51)	4 516(7)	3 254(4)	1 258(3)
C(12)	8 734(7)	9 413(4)	1 458(4)	C(52)	4 233(9)	2 744(4)	1 477(4)
C(13)	7 860(8)	9 220(5)	1 066(4)	C(53)	5 176(10)	2 459(5)	1 758(4)
C(14)	8 134(8)	8 720(5)	864(4)	C(54)	6 018(10)	2 802(5)	1 737(4)
C(15)	9 175(8)	8 590(4)	1 141(4)	C(55)	5 649(7)	3 272(4)	1 449(4)
C(16)	11 222(11)	9 158(6)	2 611(5)	C(56)	3 625(10)	4 398(5)	1 408(5)
C(17)	11 453(10)	9 810(5)	1 665(5)	C(57)	2 282(10)	3 550(6)	710(5)
C(18)	11 765(10)	8 547(5)	1 686(5)	C(58)	4 115(10)	4 104(5)	350(5)
C(21)	6 758(7)	8 812(4)	2 157(3)	C(61)	4 216(7)	1 645(4)	600(4)
C(22)	7 334(7)	8 400(4)	2 511(3)	C(62)	3 486(7)	2 103(5)	528(4)
C(23)	8 304(7)	8 616(4)	2 794(4)	C(63)	3 670(9)	2 450(5)	102(4)
C(24)	8 381(8)	9 161(4)	2 625(4)	C(64)	4 459(9)	2 194(5)	− 100(4)
C(25)	7 444(7)	9 281(4)	2 239(4)	C(65)	4 773(7)	1 728(4)	192(4)
C(26)	4 842(9)	8 056(4)	1 845(4)	C(66)	3 565(12)	452(6)	556(6)
C(27)	4 592(10)	9 268(5)	2 148(5)	C(67)	5 543(10)	791(6)	1 367(5)
C(28)	5 092(9)	8 998(5)	1 097(4)	C(68)	3 355(11)	1 135(6)	1 505(6)
C(31)	10 090(7)	6 505(4)	1 559(4)	C(71)	8 902(7)	3 438(4)	733(4)
C(32)	9 910(7)	7 018(4)	1 267(4)	C(72)	9 680(8)	3 004(4)	741(4)
C(33)	8 913(7)	7 010(4)	915(3)	C(73)	9 624(11)	2 603(5)	1 144(5)
C(34)	8 419(7)	6 494(4)	965(3)	C(74)	8 877(12)	2 795(5)	1 413(4)
C(35)	9 151(7)	6 186(4)	1 353(4)	C(75)	8 417(9)	3 288(5)	1 165(4)
C(36)	12 203(15)	5 947(7)	1 601(7)	C(76)	9 576(10)	4 095(5)	− 144(5)
C(37)	12 037(13)	6 860(7)	2 370(6)	C(77)	7 489(12)	4 358(6)	119(6)
C(38)	11 149(13)	5 721(6)	2 459(6)	C(78)	9 499(12)	4 623(6)	923(6)
C(41)	7 266(7)	6 344(4)	2 054(4)	C(81)	8 488(7)	1 822(4)	20(3)
C(42)	8 319(7)	6 123(4)	2 283(4)	C(82)	8 954(8)	2 303(4)	− 160(4)
C(43)	8 901(8)	6 502(4)	2 667(4)	C(83)	8 142(11)	2 659(5)	−453(4)
C(44)	8 227(7)	6 952(4)	2 704(3)	C(84)	7 199(10)	2 384(5)	−478(4)
C(45)	7 243(7)	6 854(4)	2 336(3)	C(85)	7 392(8)	1 892(4)	− 197(4)
C(46)	6 539(11)	5 388(5)	1 283(5)	C(86)	8 911(14)	981(7)	936(6)
C(47)	5 259(11)	5 738(6)	2 055(5)	C(87)	9 089(17)	660(8)	− 192(8)
C(48)	5 350(10)	6 491(5)	1 128(5)	C(88)	10 614(16)	1 337(9)	480(9)



Scheme 1

A similar initial oxidative addition has been proposed by Bercaw and co-workers[9b] in the reaction of [Ta(η-$C_5Me_5)_2$(=CH_2)H] with an amine affording [Ta(η-$C_5Me_5)_2$(=NR)H], and for several complexes a similar second step has been reported[5g,9b] where an imide ligand is formed from the thermolytic expulsion of R′H in alkyl amido complexes, [ML_n(NHR)R′]. Complexes **6**–**9** have been isolated by this route in good yields although variable amounts of [Nb(η-$C_5H_4SiMe_3)_2Cl_2$] were formed in the reactions with alkylamines. They have been spectroscopically characterised (see Experimental section).

An alternative route, which has been previously used[9a] for the preparation of complex **6**, has been employed to isolate **6**–**9** and consists of the thermal treatment of **2**–**5**. Hence, the imido complexes were cleanly obtained in good yields (see Experimental section) when toluene solutions of **2**–**5** were refluxed, in accordance with equation (2). The preparation of

$$[\mathrm{Nb}(\eta\text{-}C_5H_4SiMe_3)_2(\mathrm{RNCO})\mathrm{Cl}] \xrightarrow[\text{reflux}]{\text{Toluene}} [\mathrm{Nb}(\eta\text{-}C_5H_4SiMe_3)_2(=\mathrm{NR})\mathrm{Cl}] + \mathrm{CO} \quad (2)$$

6–**9**

imido derivatives by the interaction of an oxo compound with the corresponding organic isocyanate has been described,[14] and several tungsten–imidocarbonyl complexes have been prepared by the reaction of a tungsten(II) species with isocyanates,[15] but to our knowledge this is the first time that the formation of an imide ligand from the thermal treatment of a co-ordinated organic isocyanate has been described.

These complexes add to the family of the few Group 5 metal imido metallocenes which have been reported. The crystal structures of these complexes invariably indicate linear M–N–R arrangements, and bond-length arguments establish that the metal–nitrogen bond order is either three, as in [Nb(η-$C_5H_5)_2$(=NBu^t)Cl],[9d] or halfway between two and three, for example in [Ta(η-$C_5Me_5)_2$(=NPh)Cl].[9e] In order to gain more insight a crystal structure determination was undertaken for complex **6**. An ORTEP drawing of **6** is shown in Fig. 2; selected bond lengths and angles are given in Table 3 and the coordinates for all non-hydrogen atoms are in Table 4.

Compound **6** is a monomer in the solid state and it shows a typical bent-metallocene structure. Interestingly the chloride atom and the phenyl group practically lie in the equatorial plane, in a similar disposition to that found previously for $[Ta(\eta\text{-}C_5Me_5)_2(=NPh)H]$ and $[Ta(\eta\text{-}C_5Me_5)(=NH)Cl]$.[9b,9e] Using a frontier-orbital approach Jørgensen[16] explained why the phenyl group in this type of complexes lies in the equatorial plane and not perpendicular to it in an alternative arrangement. The Nb–N bond length is 1.792(2) Å, indicating that probably a bond order halfway between two, $\mathrm{Nb{=}\ddot{N}}$, and three, $\overline{\mathrm{Nb}}{\equiv}\mathrm{N}^+$, is present. However, the interesting structural parameter is the value of 165.1(2)° found for the Nb–N–C_{ipso} moiety. In the structures reported linear M–N–C geometries are observed for virtually all metallocene imido complexes thus **6** represents such an example since the deviation is about 15°. The bent arrangement could indicate that the imido nitrogen is sp^2 hybridised, but in such a case the phenyl substituent should be oriented out of the equatorial plane toward one of the cyclopentadienyl ligands.[9b] Therefore, in spite of the low angle for Nb–N–C_{ipso} we propose that the nitrogen is sp (not sp^2) hybridised and two limiting descriptions proposed by Bercaw and co-workers[9b] for $[Ta(\eta\text{-}C_5Me_5)_2(=NPh)H]$ could explain the true bonding situation.

In order to gain more insight into the nature of the Nb–N bond, extended-Hückel molecular-orbital calculations have been performed.[17,18] Fig. 3 shows an interaction diagram for the frontier orbitals of $[Nb(\eta\text{-}C_5H_5)_2(=NPh)Cl]$ from $[Nb(\eta\text{-}C_5H_5)_2Cl]^{2+}$ to the left and NPh^{2-} to the right. The results are in agreement with those found previously by Jørgensen[16] for $[Ta(\eta\text{-}C_5H_5)_2(=NPh)H]$. A Walsh diagram for five of the frontier orbitals for bending of the phenyl group in the equatorial plane between 180 and 120° is in Fig. 4, and shows that the highest occupied molecular orbital (HOMO) is unaffected by this bending in contrast to the bending out of the equatorial plane where an increase in energy similar to that

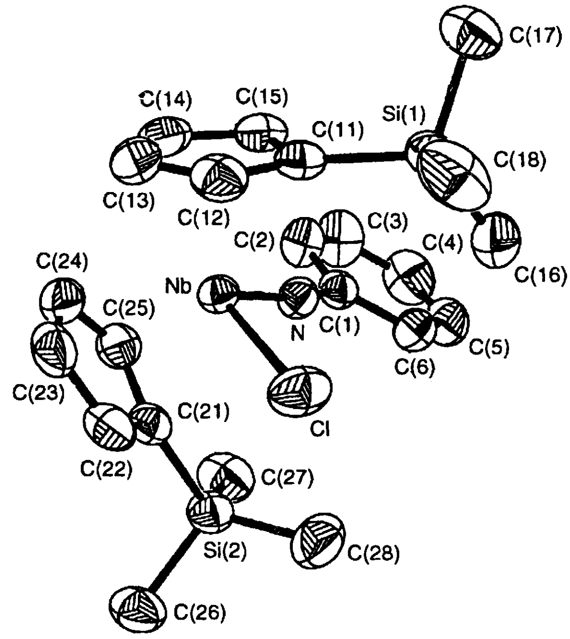
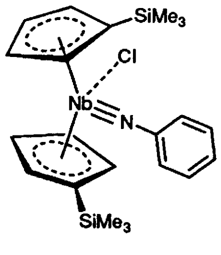
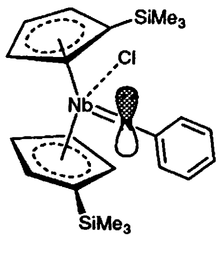


Fig. 2 An ORTEP view of the complex $[Nb(\eta\text{-}C_5H_4SiMe_3)_2(=NPh)Cl]$ **6**



$\overset{-}{\mathrm{Nb}}{\equiv}\overset{+}{\mathrm{N}}\text{–Ph}$



$\mathrm{Nb{=}\ddot{N}}\text{–Ph}$

Table 3 Selected bond lengths (Å) and angles (°) for complex **6**

Nb–N	1.792(2)	Nb–C(25)	2.424(2)
Nb–C(14)	2.433(3)	Nb–Cl(1)	2.4527(10)
Nb–C(15)	2.454(2)	Nb–C(24)	2.461(3)
Nb–C(21)	2.476(2)	Nb–C(11)	2.495(2)
Nb–C(22)	2.514(2)	Nb–C(12)	2.527(2)
Nb–C(23)	2.533(3)	Nb–C(13)	2.536(3)
Si(1)–C(16)	1.848(3)	Si(1)–C(18)	1.851(3)
Si(1)–C(17)	1.859(3)	Si(1)–C(11)	1.874(3)
Si(2)–C(28)	1.856(3)	Si(2)–C(27)	1.855(3)
Si(2)–C(26)	1.859(3)	Si(2)–C(21)	1.868(2)
N–C(1)	1.374(3)	C(1)–C(2)	1.389(4)
C(1)–C(6)	1.405(3)	C(2)–C(3)	1.381(4)
C(3)–C(4)	1.375(5)	C(4)–C(5)	1.365(5)
C(5)–C(6)	1.379(4)	C(11)–C(15)	1.404(3)
C(11)–C(12)	1.433(3)	C(12)–C(13)	1.382(4)
C(13)–C(14)	1.405(4)	C(14)–C(15)	1.405(4)
C(21)–C(22)	1.418(3)	C(21)–C(25)	1.418(4)
C(22)–C(23)	1.393(4)	C(23)–C(24)	1.394(4)
C(24)–C(25)	1.399(4)	Nb–Cp 1	2.183
Nb–Cp 2	2.176		
N–Nb–Cl	100.37(6)	C(16)–Si(1)–C(18)	111.5(2)
C(16)–Si(1)–C(17)	109.8(2)	C(18)–Si(1)–C(17)	109.2(2)
C(16)–Si(1)–C(11)	111.77(12)	C(18)–Si(1)–C(11)	108.40(14)
C(17)–Si(1)–C(11)	105.99(13)	C(28)–Si(2)–C(27)	110.7(2)
C(28)–Si(2)–C(26)	108.6(2)	C(27)–Si(2)–C(26)	110.62(14)
C(28)–Si(2)–C(21)	112.78(13)	C(27)–Si(2)–C(21)	108.41(14)
C(1)–N–Nb	165.1(2)	N–C(1)–C(2)	120.7(2)
N–C(1)–C(6)	121.2(2)	C(15)–C(11)–Si(1)	125.8(2)
C(12)–C(11)–Si(1)	128.2(2)	C(22)–C(21)–Si(2)	126.5(2)
C(25)–C(21)–Si(2)	127.7(2)	Cp 1–Nb–Cp 2	124.9
Cp 1–Nb–Cl	104.6	Cp 1–Nb–N	109.0
Cp 2–Nb–Cl	105.4	Cp 2–Nb–N	109.5

Cp 1 and Cp 2 are the centroids of the cyclopentadienyl rings.

Table 4 Atomic coordinates (× 10^4) for complex **6**

Atom	*x*	*y*	*z*
Nb	1092(1)	2216(1)	2440(1)
Cl	−2253(1)	2204(1)	2421(1)
Si(1)	−501(1)	483(1)	3512(1)
Si(2)	−178(1)	2764(1)	581(1)
N	1407(3)	1387(1)	1911(1)
C(1)	2114(3)	817(1)	1527(1)
C(2)	3993(4)	754(2)	1506(1)
C(3)	4697(5)	197(2)	1103(2)
C(4)	3558(5)	−307(2)	716(2)
C(5)	1710(5)	−255(2)	737(1)
C(6)	963(4)	292(2)	1136(1)
C(11)	1031(3)	1360(1)	3443(1)
C(12)	793(4)	2152(2)	3672(1)
C(13)	2363(4)	2587(2)	3617(1)
C(14)	3600(4)	2095(2)	3328(1)
C(15)	2811(3)	1338(2)	3253(1)
C(16)	−1285(5)	55(2)	2688(2)
C(17)	893(4)	−259(2)	4025(2)
C(18)	−2456(5)	794(2)	3954(2)
C(21)	946(3)	3040(1)	1423(1)
C(22)	190(4)	3520(2)	1899(1)
C(23)	1535(5)	3703(2)	2418(1)
C(24)	3154(4)	3333(2)	2287(1)
C(25)	2809(4)	2936(2)	1679(1)
C(26)	−937(5)	3713(2)	172(1)
C(27)	1545(5)	2268(2)	118(2)
C(28)	−2214(5)	2121(2)	616(2)

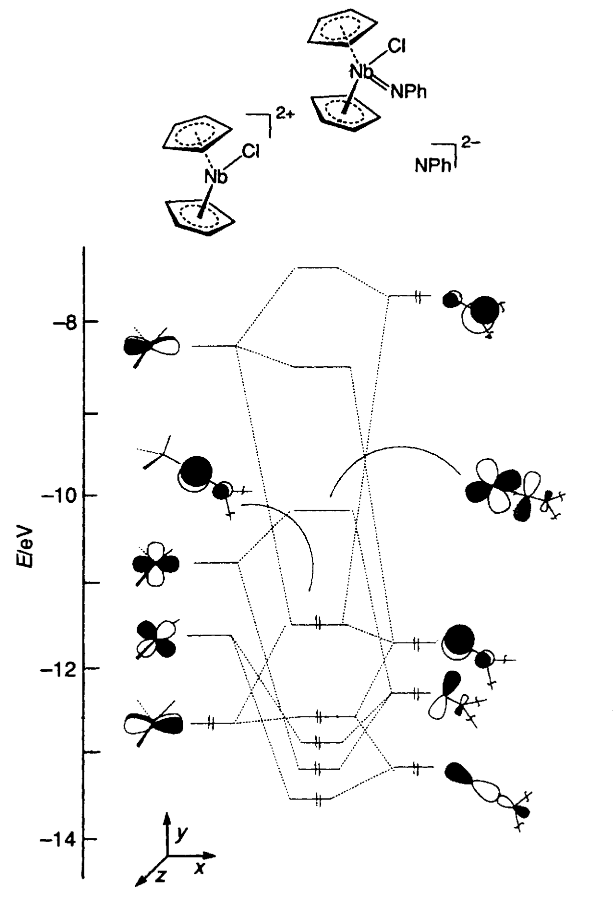


Fig. 3 Interaction diagram for the formation of [Nb(η-$C_5H_5)_2$(=NP)-Cl] from [Nb(η-$C_5H_5)_2Cl]^{2+}$ to the left and NPh^{2-} to the right. Some of the frontier orbitals are shown in the middle

described for [Ta(η-$C_5H_5)_2$(=NPh)H] is observed. However, the Walsh diagram shows that the second and third HOMO increase in energy upon bending of the phenyl group, $\theta = 140°$, and a change in the total energy from −1717.63 eV for $\theta = 180°$ to −1714.54 eV for $\theta = 120°$ is observed. However, no significant changes in energy between θ = 180 and 140° are observed, indicating that in complex **6**, with Nb–N–C_{ipso} of 165°, electronic effects are not responsible. The Nb–N and N–C_{ipso} overlap populations decrease as a result of the bending and the charge at niobium decreases as the nitrogen charge increases (see Table 5). The phenyl substituent arranges itself so as to maximise the overlap with the nitrogen p orbital, but slight modifications of this overlap are observed in the range θ = 180–160°. We have established that the imido bond angles for 'linear imide' in this class of complexes can vary until 140° with little efect on the M–N bonding.

Experimental

General Procedures.—All manipulations were performed using standard, Schlenk techniques in an atmosphere of dry, oxygen-free nitrogen or argon. Solvents were distilled from appropriate drying agents and degassed before use. The C, H, N analyses were carried out with a Perkin-Elmer 240 B microanalyser. Proton and ^{13}C NMR spectra were recorded on an Unity Varian 300 instrument and referenced to the residual deuteriated solvent, infrared spectra as Nujol mulls between CsI plates in the region 4000–200 cm^{-1} with a Perkin-Elmer 883 spectrometer. The isocyanate and amine derivatives are commercially available. The molecular-orbital calculations were carried out using the CACAO program.[17] We have used the data from the crystal structure of complex **6**.

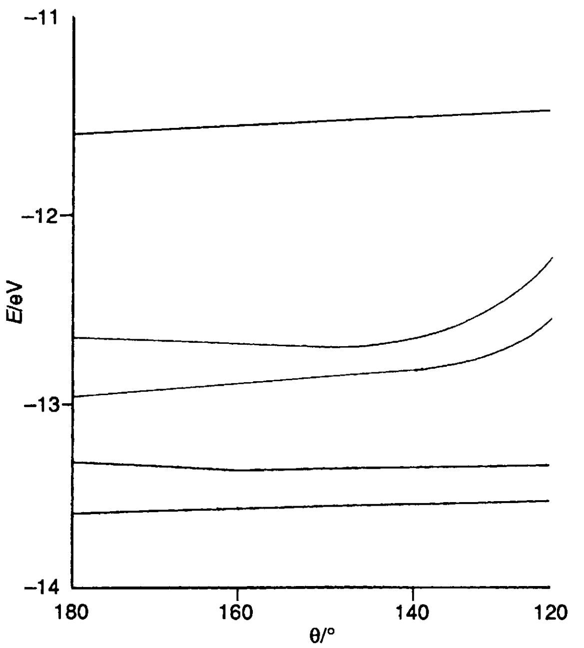


Fig. 4 Walsh diagram for the bending of the phenyl group in the equatorial plane

Preparation of [Nb(η-$C_5H_4SiMe_3)_2$(RNCO)Cl] (R = Ph **2**, Bu^t **3**, Pr^n **4** *or* Pr^i **5**).—The chemical procedure was similar in all cases. To a solution in pentane (50 cm^3) of [Nb(η-$C_5H_4SiMe_3)_2Cl$] (0.64 g, 1.94 mmol) was added an equimolar quantity of the corresponding isocyanate. The mixture was vigorously stirred overnight at room temperature after which a yellowish-white microcrystalline precipitate was obtained. This was filtered off and dried under vacuum. Yield *ca* 80% [Found (calc.): **2**, C, 52.55 (52.95); H, 5.95 (6.00); N, 2.90 (2.70). **3**, C, 50.40 (50.30); H, 6.90 (7.05); N, 2.95 (2.80). **4**, C, 49.50 (49.25); H, 6.75 (6.85); N, 3.15 (2.85). **5**, C, 49.30 (49.25); H, 6.70 (6.85); N, 3.00 (2.85)%]. IR [ν(C=O) or ν(C=N)]: **2**, 1721; **3**, 1781; **4**, 1759; **5**, 1778 cm^{-1}. NMR (C_6D_6): ^1H, **2**, δ 0.17 (s, $SiMe_3$), 5.25(1), 5.38(1) 6.00(1), 6.13(1) (m, $C_5\mathit{H}_4SiMe_3$) 6.89 (m), 7.25 (m) and 8.43 (d) (C_6H_5); **3**, δ 0.27 (s, $SiMe_3$), 0.89 [s, $(CH_3)_3C$]; 5.32(1), 5.52(1), 5.77(1) and 6.00(1) (m, $C_5\mathit{H}_4SiMe_3$); **4**, δ 0.26 (s, $SiMe_3$), 0.84 (t, $C\mathit{H}_3CH_2CH_2$), 1.60 (m, $CH_3C\mathit{H}_2CH_2$ and 3.35 (t, $CH_3CH_2C\mathit{H}_2$); **5**, δ 0.27 (s, $SiMe_3$), 1.28 [d, $(C\mathit{H}_3)_2CH$–], 4.16 [m, $(CH_3)_2C\mathit{H}$–], 5.35 (1) and 5.64(3) (m, $C_5\mathit{H}_4SiMe_3$); ^{13}C-{^1H}, **2**, δ − 0.23($SiMe_3$), 105.7, 109.5, 116.1 (C_{ipso}), 119.0, 121.2 ($\mathit{C}_5H_4SiMe_3$), 124.0, 124.4, 144.1 (C_{ipso}) (C_6H_5) and 187.2 (NCO); **3**, δ 0.03 ($SiMe_3$), 30.0 [$(\mathit{C}H_3)_3C$], 58.0 [$(CH_3)_3\mathit{C}$], 110.2, 112.6, 113.0 (C_{ipso}), 118.8, 127.7 ($\mathit{C}_5H_4SiMe_3$) and 179.6 (NCO); **4**, −0.81($SiMe_3$), 11.6 ($\mathit{C}H_3CH_2CH_2$); 21.8 ($CH_3\mathit{C}H_2CH_2$), 42.2 ($CH_3CH_2\mathit{C}H_2$), 105.6, 109.2, 113.8 (C_{ipso}), 116.7, 117.2 ($\mathit{C}_5H_4SiMe_3$) and 181.7 (NCO); **5**, 0.01 ($SiMe_3$), 21.6 [$(\mathit{C}H_3)_2CH$]; 44.7 [$(CH_3)_2\mathit{C}H$], 108.6, 110.9, 113.8 (C_{ipso}), 114.0, 118.4 ($\mathit{C}_5H_4SiMe_3$) and 180.5(NCO).

Preparation of [Nb(η-$C_5H_4SiMe_3)_2$(=NR)Cl] (R = Ph **6**, Bu^t **7**, Pr^n **8** *or* Pr^i **9**).—*Method A: thermal decomposition of the corresponding isocyanate derivatives.* The chemical procedure was similar in all cases. A solution of complex **2** (**3**, **4** or **5**) in toluene was stirred under reflux overnight. The initial pale yellow solution turned red. After concentration to dryness, extraction with pentane, concentration and cooling at −30 °C, red-orange crystals of [Nb(η-$C_5H_4SiMe_3)_2$(=NR)Cl] (R = Ph **6**, Bu^t **7**, Pr^n **8** or Pr^i **9**) were obtained. Yield 60–70%.

Method B: reaction of complex **1** *with the corresponding amine derivatives.* The chemical procedure was similar in all cases.

Table 5 Values for the overlap populations of the N–C and Nb–N bonds and charges (N, Nb) as a function of the bending angle Nb–N–C(Ph) in the equatorial plane

Angle θ (in the plane)/°	120	140	160	180
Energy/eV	−1714.54	−1716.84	−1717.50	−1717.63
Overlap population (N–C bond)	797	836	857	862
Charge on N	−1.091	−0.894	−0.806	−0.786
Charge on Nb	0.840	0.623	0.531	0.512
Overlap population (Nb–N bond)	895	978	1017	1030

Table 6 Crystal and X-ray structural analysis data for compounds **1** and **6** *

	1	**6**
Empirical formula	$C_{32}H_{52}Cl_2Nb_2Si_4$	$C_{22}H_{31}ClNNbSi_2$
M	805.8	494.02
Crystal colour, habit	Reddish brown, prism	Red-orange, prism
Crystal system, space group	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/n$
a,b,c/Å	12.968(4), 23.988(7), 25.546(7)	7.343(2), 16.880(3), 20.227(4)
β/°	103.22(3)	96.41(2)
U/Å^3,Z	7736(4), 8	2491.4(10), 4
D_c/g cm^{-3}	1.384	1.317
μ(Mo-$K\alpha$)/cm^{-1}	8.74	6.94
$F(000)$	3328	1024
Reflections measured	12 905	4780
Unique reflections	12 057	4300
hkl ranges	0–14, 0–27, −29 to 29	0–8, 0–20, −24 to 24
Number of parameters refined	601	265
Goodness of fit	1.129	1.094
$R1 = \Sigma\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert/\Sigma\lvert F_o\rvert]$	0.060	0.026
$wR2 = [\lvert\Sigma(F_o^2 - F_c^2)^2\rvert/\lvert\Sigma w(F_o^2)^2\rvert]^{\frac{1}{2}}$	0.146	0.065
Weighting scheme, w where $P = (F_o^2 + 2F_c^2)/3$	$1/[\sigma^2(F_o^2) + (0.0830P)^2 + 22.7344P]$	$1/[\sigma^2(F_o^2) + (0.0334P)^2 + 1.0794P]$
Largest difference peak and hole/e Å^{-3}	1.169, −0.901	0.544, −0.415

* Details in common: cell dimensions from least-squares fit of 25 reflections having $\theta < 12°$; four-circle diffractometer; bisecting geometry, graphite-oriented monochromator; ω–θ scan mode; $R1$ is defined for reflections with $F > 4\sigma(F)$ and $wR2$ for all data.

A solution of complex **1** (0.84 g, 2.08 mmol) in hexane was stirred with aniline (0.19 cm^3; 1.022 g cm^{-3}, 2.09 mmol) under mild pressure [*ca.* 4 atm ($\approx 4 \times 10^5$ Pa)] overnight. After concentration to dryness, extraction with pentane, concentration and cooling at −30° C, red-orange crystals of complex **6** were obtained. When Bu^tNH_2, Pr^nNH_2 or Pr^iNH_2 was used complex **7**, **8** or **9** was isolated. Yield *ca.* 70% [Found (calc.): **6**, C, 53.10 (53.55); H, 6.25 (6.35); N, 2.95 (2.85). **7**, C, 50.50 (50.75); H, 7.50 (7.45); N, 3.00 (2.95); **8**, C, 49.60 (49.65); H, 7.35 (7.25); N, 3.05 (3.05); **9**, C, 49.00 (49.65); H, 7.15 (7.25); N, 3.15 (3.05)%]. NMR (C_6D_6): ^{1}H, **6**, δ 0.26 (s, $SiMe_3$), 5.53(1), 5.97(1), 6.26(1), 6.35(1) (m, $C_5H_4SiMe_3$), 6.50 (d, $^3J_{HH}$ = 8, *o*-H of Ph), 6.70 (t, $^3J_{HH}$ = 8, *m*-H of Ph), and 7.10 (t, $^3J_{HH}$ = 8 Hz, *p*-H of Ph); **7**, δ 0.34 (s, $SiMe_3$), 1.02 [s, $(CH_3)_3C$], 5.91(1), 6.25(1), 6.31(1) and 6.40(1) (m, $C_5H_4SiMe_3$); **8**, δ, 0.35 (s, $SiMe_3$); 1.05 (t, $CH_3CH_2CH_2$), 1.45 (m, $CH_3CH_2CH_2$), 3.63 (t, $CH_3CH_2CH_2$), 5.63(1) and 6.13(3) (m, $C_5H_4SiMe_3$); **9**, δ, 0.33 (s, $SiMe_3$), 1.09 [d, $(CH_3)_2CH$], 3.83 [m, $(CH_3)_2CH$], 5.79(1) and 6.10(3) (m, $C_5H_4SiMe_3$); ^{13}C-{^{1}H}, **6**, δ 0.23 ($SiMe_3$), 110.7, 111.1, 119.6 (C_{ipso}), 119.9, 127.1 ($C_5H_4SiMe_3$), 118.2, 121.7, 128.0 and 159.9 (C_{ipso}) (C_6H_5); **7**, δ 0.20 ($SiMe_3$), 30.0 [$(CH_3)_3C$], 67.6 [$(CH_3)_3C$], 112.4, 114.3 (C_{ipso}), 115.9, 119.1 and 123.3 ($C_5H_4SiMe_3$); **8**, δ 0.18 ($SiMe_3$), 12.5 ($CH_3CH_2CH_2$), 28.6 ($CH_3CH_2CH_2$), 45.4 ($CH_3CH_2CH_2$), 111.2 (C_{ipso}); 112.3, 113.4 and 121.4 ($C_5H_4SiMe_3$); **9**, δ −0.04 ($SiMe_3$), 23.7 [$(CH_3)_2CH$], 66.9 [$(CH_3)_2CH$)]; 111.9, 120.2 (C_{ipso}), 122.1 and 125.3 ($C_5H_4SiMe_3$).

Crystal Structure Analyses of Complexes **1** *and* **6**.—Intensity data were collected on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo-Kα radiation (λ 0.710 73 Å). Two check reflections were monitored every 120 min and showed no significant variations. All intensity data were corrected for Lorentz polarisation effects, but it was not necessary to apply any absorption correction. Crystal data and a summary of data collection and structure parameters are given in Table 6. Calculations were carried out on an ALPHA AXP(digital) workstation.

The structures were solved by direct methods (SHELXS 90)[19] and refined by least squares against F^2 (SHELXL 93).[20] All non-hydrogen atoms were refined anisotropically and the hydrogen atoms were positioned geometrically and refined using a riding model with a fixed thermal parameter (U = 0.08 Å^2).

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

Acknowledgements

We gratefully acknowledge financial support from the Direccion General de Investigación Científica y Técnica (DGICyT) (Grant No. PB92-0715) and Universidad de Alcalá de Henares (P. G.-S. and A. M.-A., 94/4).

References

1 R. Aumann, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 1456; G. L. Geoffroy and S. L. Bassner, *Adv. Organomet. Chem.*, 1988, **28**, 1; D. J. Darensbourg and R. A. Kudaroski, *Adv. Organomet. Chem.*, 1983, **22**, 129; A. Behr, *Carbon Dioxide Activation by Metal Complexes*, VCH, Weinheim, 1988.

2 (*a*) G. Chandra, A. D. Jenkins, M. F. Lappert and R. C. Srivastava, *J. Chem. Soc. A*, 1970, 2550; (*b*) J. D. Wilkins, *J. Organomet. Chem.*, 1974, **65**, 383; (*c*) J. D. Wilkins, *J. Organomet. Chem.*, 1974, **67**, 269; (*d*) G. Fachinetti, C. Brian, C. Floriani, A. Chiesi-Villa and C. Guastini, *J. Chem. Soc., Dalton Trans.*, 1979, 792; (*e*) P. Braunstein, D. Matt and D. Nobel, *Chem. Rev.*, 1989, **89**, 1927.

3 J. P. Collman, M. Kubota, F. D. Vastine, J. Sun and J. W. Kang, *J. Am. Chem. Soc.*, 1968, **90**, 5430; G. La Monica, S. Cenini and M. Freni *J. Organomet. Chem.*, 1974, **76**, 355; S. Cenini, M. Pizzotti, F. Porta and G. La Monica, *J. Organomet. Chem.*, 1975, **88**, 237; R. Richards and G. Rouschias, *J. Am. Chem. Soc.*, 1976, **98**, 5279; H. Hasegawa, K. Itoh and Y. Ishii, *Inorg. Chem.*, 1974, **13**, 2675; S. Otsuka, A. Nakamura and Y. Tatsumo, *J. Am. Chem. Soc.*, 1969, **91**, 6994; H. Hoberg and J. Korff, *J. Organomet. Chem.*, 1978, **150**, C20.

4 W. A. Nugent and J. M. Mayer, *Metal–Ligand Multiple Bonds*, Wiley-Interscience, New York, 1988; W. A. Nugent and B. L. Haymore, *Coord. Chem. Rev.*, 1980, **31**, 125.

5 (*a*) C. C. Cummins, S. M. Baxter and P. T. Wolczanski, *J. Am. Chem. Soc.*, 1988, **110**, 8731; (*b*) P. J. Walsch, F. J. Hollander and R. G. Bergman, *J. Am. Chem. Soc.*, 1988, **110**, 8729; (*c*) C. C. Cummins, C. P. Schaller, G. D. Van Duyne, P. T. Wolczanski, A. W. E. Chan and R. Hoffman, *J. Am. Chem. Soc.*, 1991, **113**, 2985; (*d*) D. S. Glueck, J. Wu, F. J. Hollander and R. G. Bergman, *J. Am. Chem. Soc.*, 1991, **113**, 2041; (*e*) T. R. Cundari, *J. Am. Chem. Soc.*, 1992, **114**, 10557; (*f*) P. J. Walsch, A. M. Baranger and R. G. Bergman, *J. Am. Chem. Soc.*, 1992, **114**, 170; (*g*) J. de With and A. D. Horton, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 903.

6 D. S. Glueck, F. J. Hollander and R. G. Bergman, *J. Am. Chem. Soc.* 1989, **111**, 2719; R. I. Michelman, R. A. Andersen and R. G. Bergman, *J. Am. Chem. Soc.*, 1991, **113**, 5100; M. H. Schofield, T. P. Kee, J. T. Anhaus, R. R. Schrock, K. H. Johnson and W. M. Davis, *Inorg. Chem.*, 1991, **30**, 3595.

7 See, for example, W. A. Nugent, *Inorg. Chem.*, 1983, **22**, 965; D. C. Bradley, M. B. Hursthouse, K. M. Abdul Malik, A. J. Nielson and G. B. Chota-Vuru, *J. Chem. Soc., Dalton Trans.*, 1984, 1069; P. A. Bates, A. J. Nielson and J. M. Waters, *Polyhedron*, 1985, **4**, 1391; Y.-W. Chao, P. A. Wexler and D. E. Wigley, *Inorg. Chem.*, 1989, **28**, 3860; 1990, **29**, 4592; J. de With and A. D. Horton, *Organometallics*, 1990, **9**, 2207; D. P. Smith, K. D. Allen, M. D. Carducci and D. E. Wigley, *Inorg. Chem.*, 1992, **31**, 1319.

8 See, for example, D. N. Williams, J. P. Mitchell, A. D. Poole, U. Siemeling, W. Clegg, D. C. R. Hockless, P. A. O'Neil and V. C. Gibson, *J. Chem. Soc., Dalton Trans.*, 1992, 739; U. Siemeling and V. C. Gibson, *J. Organomet. Chem.*, 1992, **426**, C25–C27; V. C. Gibson, A. D. Poole, U. Siemeling, D. N. Williams, W. Clegg and D. C. R. Hockless, *J. Organomet. Chem.*, 1993, **462**, C12–C14; T. C. Baldwin, S. R. Huber, M. A. Bruck and D. E. Wigley, *Inorg. Chem.*, 1993, **32**, 5682.

9 (*a*) A. Antiñolo, S. Garcia-Lledó, J. Martinez de Ilarduya and A. Otero, *J. Organomet. Chem.*, 1987, **335**, 85; (*b*) G. Parkin, A. Van Asselt, D. J. Leahy, L. R. Whinnery, N. G. Hua, R. W. Quan, L. M. Henling, W. P. Schaefer, B. D. Santarsiero and J. E. Bercaw, *Inorg. Chem.*, 1992, **31**, 82; (*c*) M. L. H. Green, D. M. Michaelidou, P. Mountford, A. G. Suarez and L.-L. Wong, *J. Chem. Soc., Dalton Trans.*, 1993, 1593; (*d*) A. N. Chernega, M. L. H. Green and A. G. Suarez, *J. Chem. Soc., Dalton Trans.*, 1993, 3031; (*e*) D. M. Antonelli, W. P. Schaefer, G. Parkin and J. E. Bercaw, *J. Organomet. Chem.*, 1993, **462**, 213; (*f*) J. Schmidt and J. Sundermeyer, *J. Organomet. Chem.*, 1994, **472**, 127.

10 A. Antiñolo, M. Fajardo, C. López-Mardomingo, A. Otero, Y. Mourad, Y. Mugnier, J. Sanz-Aparicio, I. Fonseca and F. Florencio, *Organometallics*, 1990, **9**, 2919; A. Antiñolo, A. Otero, M. Fajardo, C. López-Mardomingo, D. Lucas, Y. Mugnier, M. Lanfranchi and M. A. Pellinghelli, *J. Organomet. Chem.*, 1992, **435**, 55.

11 G. A. Luinstra and J. H. Teuben, *J. Chem. Soc., Chem. Commun.*, 1990, 1470; J. W. Pattiasina, H. J. Heeres, F. van Bohuis, A. Meetsma, J. H. Teuben and A. L. Spek, *Organometallics*, 1987, **6**, 1004.

12 C. K. Johnson, ORTEP, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.

13 W. J. Evans, T. T. Peterson, M. D. Rausch, W. E. Hunter, H. Zhang and J. L. Atwood, *Organometallics*, 1985, **3**, 554.

14 I. S. Kolomnikov, Y. D. Koreshkov, T. S. Lobeeva and M. E. Volpin, *Chem. Commun.*, 1970, 1432; D. C. Bradley, M. B. Hursthouse, K. M. Abdul Malik, A. J. Nielson and R. L. Short, *J. Chem. Soc., Dalton Trans.*, 1983, 2651; G. Schoettel, J. Kress and J. A. Osborn, *J. Chem. Soc., Chem. Commun.*, 1989, 1062.

15 F.-M. Su, J. C. Bryan, S. Jang and J. M. Mayer, *Polyhedron*, 1989, **8**, 1261.

16 K. A. Jørgensen, *Inorg. Chem.*, 1993, **32**, 1521.

17 C. Mealli, *J. Chem. Educ.*, 1990, **67**, 399.

18 R. Hoffmann, *J. Chem. Phys.*, 1963, **39**, 1379; (*b*) R. Hoffmann and W. N. Lipscomb, *J. Chem. Phys.*, 1962, **36**, 2179; **37**, 2872.

19 G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 1990, **46**, 467.

20 G. M. Sheldrick, SHELXL 93, University of Göttingen, 1993.

Received 25*th October* 1994; *Paper* 4/06530A