Further studies of the reactivity of cyclopentadienyl, substituted cyclopentadienyl and indenyl ligands with $M_2Cl_2(NMe_2)_4$ (M = Mo or W). Crystal and molecular structures of $Mo_2(C_9H_7)_2(NMe_2)_4$ and $W_2(C_5H_4Me)_2(NMe_2)_4$ †

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Metathetic reactions employing 1,2-$M_2Cl_2(NMe_2)_4$ compounds (M = Mo or W) and the sodium or lithium salts of cyclopentadienyl (Cp), methylcyclopentadienyl, indenyl (C_9H_7) and bis(methyl)bis(cyclopentadienyl)silyl, $Me_2Si(C_5H_4)_2{}^{2-}$, anions carried out in hydrocarbon or ether solvents have led to the isolation of orange, hydrocarbon-soluble, air-sensitive crystalline solids of formula 1,2-$M_2R_2(NMe_2)_4$. In solution the NMR data are consistent with C_2 symmetry and restricted rotation about the M–N bonds. The complexes where R = C_5H_5 show only one CH resonance in their ^{1}H NMR spectra consistent with ring whizzing. The solid-state and molecular structures of $Mo_2(C_9H_7)_2(NMe_2)_4$ and $W_2(C_5H_4Me)_2(NMe_2)_4$ reveal that the indenyl and C_5H_4Me ligands are η^3-bonded to the M≡M^{6+} moiety with three M–C distances within the range 2.35 to 2.52 Å and two distinctly larger, *ca.* 2.75–2.80 Å. The M–M distances, 2.252(1) Å (M = Mo) and 2.345(1) Å (M = W) and M–N distances, 1.96 to 1.99 Å, are similar to those for 1,2-$M_2R_2(NMe_2)_4$ compounds, where R = alkyl or aryl. The linked Cp complex $W_2[(C_5H_4)_2SiMe_2](NMe_2)_4$ was found to show similar structural features although the molecular structure suffered from disorder. The data reported, together with previous results, show that cyclopentadienyl ligands compete favorably with the NMe_2 ligand as $\sigma^2\pi^2$ donors, η^3-C_5. The η^5-C_5 mode is not favoured (on electronic grounds) because this would require disruption of the M–M triple bond in the presence of four Me_2N $\sigma^2\pi^2$ donors.

The first members of the now extensive class of M_2X_6 or $M_2X_{6-n}Y_n$ compounds, where n = 1, 2 or 3 and M = Mo or W,[1] were prepared by Wilkinson and co-workers,[2] $M_2(CH_2SiMe_3)_6$, and structurally characterized later.[3] The salient feature of these ethane-like M–M triply bonded compounds is that the groups X (or X and Y) must provide sufficient bulk to suppress dimerization to give M_4 clusters (or oligomerization to higher nuclearity species).‡,[4] Also, in so much as the formation of three metal–ligand σ bonds and the M–M triple bond provides only 12 valence electrons per metal atom, π-donor ligands such as amides, alkoxides, *etc.* are desirable. These act as π buffers for otherwise electron-deficient and Lewis acidic metal centers.[5] Because of the C_3 axis of symmetry the metal d_π orbitals fall into two classes both having e symmetry, only one of which can form the M–M π bond. Consequently there is a mutual competition between M–M and M–L π bonding and ligands such as NR_2, which are single faced π donors, align their NC_2 blades along the M–M axis so that M–NR_2 π bonding involves exclusively the in-plane metal d_π orbitals (d_{xy}, $d_{x^2-y^2}$).[6] This results in restricted rotation about the M–N bond and for compounds of the type 1,2-$M_2X_2(NMe_2)_4$ one can measure the relative π-donor properties of X and NMe_2 by both structural parameters and rotational barriers. In this way one can determine the relative π-donor properties of X, *e.g.* X = NMe_2 > OR > OPh ≈ $OSiR_3$ > Cl.[7] Ligands such as PR_2 and AsR_2 are shown to be poorer π donors than NR_2 ligands and are pyramidal at P or As and may form bridged structures as in $W_2(\mu\text{-PPh}_2)_2(NMe_2)_4$.[8,9]

We were interested in how η^n-hydrocarbyl ligands such as allyl, cyclopentadienyl (Cp), indenyl (C_9H_7), cycloocta-1,5-diene (COT), *etc.* would co-ordinate to the $M_2{}^{6+}$ center in the presence of NMe_2 ligands and earlier work has shown that allyl[10] and COT[11] may act as π acceptors and π donors by adopting bridging positions. In these cases the M–M π bonding is partially disrupted. However, for $W_2[H_2C=C(Me)CH_2]_2$-$(NMe_2)_4$ the allyl ligand was seen to be η^1-CH_2CMeCH_2[10] and the central $W_2C_2(N)_4$ core was similar to those of 1,2-$M_2R_2(NMe_2)_4$ complexes, where R = alkyl or aryl.[12] In the case of X = Cp we were unable to establish the mode of bonding while for $W_2(C_9H_7)_2(NMe_2)_4$ an η^3-C_9H_7 co-ordination was seen.[13] We describe here further studies of the preparation and characterization of cyclopentadienyl and indenyl complexes of dimolybdenum and ditungsten supported by four NMe_2 ligands which reveal that the Cp and indenyl ligands compete effectively with the NMe_2 ligands as $\sigma^2\pi^2$ donors.

Experimental

Details of our general experimental procedures have been given in previous papers.[13] All manipulations were performed under an atmosphere of dry nitrogen or argon and solvents were dried and distilled from sodium benzophenone prior to use. The complex 1,2-$W_2Cl_2(NMe_2)_4$ was synthesized by a literature method,[14] and $Li_2[(C_5H_4)_2SiMe_2]$ was prepared from the reaction between Me_2SiCl_2 and NaC_5H_5 in Et_2O at 0 °C followed by the addition of *n*-butyllithium (2 equivalents). The salt $Na(C_5H_4Me)$ was prepared from C_5H_5Me and NaH in diethyl ether at 0 °C. Proton and ^{13}C NMR spectra were recorded on Varian XL300 and Bruker AM500 instruments. Variable-temperature ^{1}H NMR were recorded at 300 MHz. Temperatures were calibrated using ethylene glycol. Infrared spectra were measured on Perkin-Elmer 283 and Nicolet 510 P FT-IR instruments.

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† In memory of Sir Geoffrey Wilkinson, an inspirational chemist and teacher.

‡ For example, as in the coupling of $M_2(OR)_6$ compounds to give $M_4(OR)_{12}$ clusters.

Table 1 Summary of crystal data

	$C_{26}H_{38}Mo_2N_4$	$C_{20}H_{38}N_4W_2 \cdot 0.5C_7H_8$
Empirical formula		
Molecular weight	598.49	1496.63
Color of crystal	Black	Yellow
Crystal dimensions/mm	$0.25 \times 0.24 \times 0.25$	$0.24 \times 0.24 \times 0.16$
Space group	$P\bar{1}$	$P\bar{1}$
$T/^\circ C$	-155	-160
$a/\text{Å}$	13.488(3)	10.445(3)
$b/\text{Å}$	10.785(2)	13.736(3)
$c/\text{Å}$	9.469(1)	9.846(2)
$\alpha/^\circ$	81.30(1)	104.20
$\beta/^\circ$	84.64(1)	100.60(1)
$\gamma/^\circ$	105.14(1)	67.67(1)
Z	2	1
$U/\text{Å}^3$	1301.53	1261.52
$D_c/\text{g cm}^{-3}$	1.527	1.970
$\lambda/\text{Å}$	0.710 69	0.710 69
μ/cm^{-1}	9.604	93.254
Detector to sample distance/cm	22.5	22.5
Sample to source distance/cm	23.5	23.5
Average ω scan width at half height/$^\circ$	0.25	0.25
Scan speed/$^\circ$ min^{-1}	4.0	6.0
Scan width/$^\circ$ (+dispersion)	2.0	2.5
Individual background/s	4	6
Aperture size/mm	3.0×4.0	3.0×4.0
2θ Range/$^\circ$	6–45	6–45
Total no. of reflections collected	4002	4922
no. of unique intensities	3413	3310
no. with $F > 2.33\sigma(F)$	3073	2348
$R(F)$	0.0285	0.0405
$R'(F)$	0.0332	0.0431
Goodness of fit for last cycle	0.952	1.055
Maximum δ/σ for last cycle	0.05	0.06

Synthesis of $W_2[(C_5H_4)_2SiMe_2](NMe_2)_4$

To a stirred solution of $1,2\text{-}W_2Cl_2(NMe_2)_4$ (0.62 g, 1.0 mmol) in tetrahydrofuran (thf) (35 cm³) at room temperature Li_2-$[(C_5H_4)_2SiMe_2]$ (0.21 g, 1.05 mmol) was added from a solids addition tube. After 15 h the solvent was removed *in vacuo*. The residue was extracted with CH_2Cl_2 and filtered through Celite® on a medium porosity frit. Dichloromethane was removed *in vacuo* and the residue crystallized from 1,2-dimethoxyethane at $-20\,^\circ C$ (yield of yellow crystals, 0.4 g, 55% based on tungsten) [Found: C, 32.82; H, 5.42; N, 7.76. Calc. for $C_{20}H_{38}N_4SiW_2$ (730.33): C, 32.89; H, 5.24; N, 7.67%]. IR (KBr pellet)/cm^{-1}: 2964w (br), 2851s, 2808s, 2764vs, 1449w, 1414w, 1358vw, 1242ms, 1201vw, 1169w, 1142w, 1123vw, 1044ms, 961s, 943vs, 893w, 826m, 801s, 772s, 669w, 550w, 467w, 411w. ^{1}H NMR (C_6D_6 at 23 °C and 500 MHz, *gauche* rotamer): δ 0.74 {s, 6 H, CH_3 of $[(C_5H_4)_2SiMe_2]$}, 2.59 [br, 12 H, $N(CH_3)_2$], 4.16 [br, 6 H, $N(CH_3)_2$], 4.27 [br, 6 H, $N(CH_3)_2$], multiplets centered at 5.54, 6.19, 6.22 and 7.05 {C_5H_4 of $[(C_5H_4)_2SiMe_2]$}; (-73.6 °C, *gauche* rotamer) δ 0.81 {s, 6 H, CH_3 of $[(C_5H_4)_2SiMe_2]$}, 4.38 [s, 6 H, $N(CH_3)_2$], 4.19 [s, 6 H, $N(CH_3)_2$], 2.60 [s, 6 H, $N(CH_3)_2$], 2.55 [s, 6 H, $N(CH_3)_2$], multiplets centered at 5.42, 6.11, 6.14 and 7.05 {C_5H_4 of $[(C_5H_4)_2SiMe_2]$}.

Synthesis of $W_2(C_5H_4Me)_2(NMe_2)_4$

To a stirred solution of $Na(C_5H_4Me)$ (0.36 g, 3.53 mmol) in diethyl ether (30 cm³) at room temperature, $W_2Cl_2(NMe_2)_4$ (1.0 g, 1.63 mmol) was added from a solids addition tube (1 h). The reaction mixture was stirred for 6 h. The solvent was removed *in vacuo*. The residue was extracted with hexane and filtered through Celite® on a medium porosity frit. Hexane was removed *in vacuo* and the residue was recrystallized from toluene at $-20\,^\circ C$ (yield 0.61 g, 53.5% based on W) [Found: C, 34.07; H, 5.53; N, 7.89. Calc. for $C_{20}H_{38}N_4W_2$ (701.7): C, 34.20; H, 5.41; N, 7.98%]. IR (Nujol mull between CsI plates)/cm^{-1}: 3035vw (br), 2954w, 2834ms (br), 2809ms, 2766ms, 1498m, 1448ms, 1422w, 1413ms, 1382m, 1367w, 1239s, 1143ms, 1137ms, 1129m, 1075w, 1040ms, 1021m, 962vs, 946vs,

840w, 827m, 806s, 792vs, 782s, 602w, 545s, 347m (br), 300vw. ^{1}H NMR (C_6D_6 at 23 °C and 300 MHz): δ 1.81 [s, 6 H, CH_3 of (C_5H_4Me)], 2.70 [br, 12 H, $N(CH_3)_2$], 4.32 [br, 12 H, $N(CH_3)_2$], multiplets centered at 5.87, 6.27 and 6.94 [C_5H_4 of (C_5H_4Me)]; ([$^2H_8$]toluene at -78 °C) δ 1.82 [s, 6 H, CH_3 of (C_5H_4Me)], 2.59 and 2.70 [s, 12 H, $N(CH_3)_2$], 4.16 and 4.47 [s, 12 H, $N(CH_3)_2$], multiplets centered at 5.62, 5.86, 6.13 and 7.09 [$C_5H_4(C_5H_4Me)$].

Synthesis of $Mo_2(C_9H_7)_2(NMe_2)_4$

To a well stirred solution of $Li(C_9H_7)$ (0.44 g, 3.6 mmol) in diethyl ether (30 cm³) at room temperature was added 0.749 g (1.7 mmol) of $Mo_2Cl_2(NMe_2)_4$ from a solids addition tube over 2 h. After a further 4 h of stirring the solvent was removed *in vacuo*. The residue was extracted with hexane and filtered through Celite® on a fine porosity frit. Hexane was removed *in vacuo* to give a crystalline solid which was recrystallized from toluene at $-15\,^\circ C$ (yield of orange crystals, 0.58 g, 57% based on tungsten) [Found: C, 52.43; H, 6.47; N, 9.28. Calc. for $C_{26}H_{38}Mo_2N_4$ (598.4): C, 52.08; H, 6.36; N, 9.36%]. IR (Nujol mull between CsI plates)/cm^{-1}: 3050vw, 2775w, 1603m, 1425 (sh), 1419m, 1395w, 1391 (sh), 1334ms, 1245ms, 1147ms, 1119ms, 1075m, 1049ms, 1033m, 1009ms, 960ms, 950ms, 888w, 878m, 860ms, 855m, 848m, 809ms, 783ms, 753ms, 743ms, 696vw, 562vs (br), 452vs, 402s, 367vs (br), 303w, 235s, 224vs. ^{1}H NMR ([$^2H_8$]toluene at 20 °C and 300 MHz, *gauche* rotamer): δ multiplets centered at 7.80 (1 H), 7.47 (1 H), 7.22 (1 H), 6.86 (2 H), 6.79 (1 H) and 6.62 (1 H) (C_9H_7), 3.87 and 2.04 [br, 12 H, $N(CH_3)_2$]; (-60 °C, *gauche* rotamer) δ 4.06 [s, 6 H, $N(CH_3)_2$], 3.91 [s, 6 H, $N(CH_3)_2$], 2.09 [s, 6 H, $N(CH_3)_2$], 1.60 [s, 6 H, $N(CH_3)_2$], multiplets centered at 8.04 (1 H), 7.52 (1 H), 7.21 (1 H), 6.93 (2 H), 6.80 (1 H) and 6.47 (1 H) (C_9H_7).

Synthesis of $Mo_2(C_5H_5)_2(NMe_2)_4$

To a well stirred slurry of $Na(C_5H_5)$ (0.32 g, 3.6 mmol) in toluene (50 cm³) at room temperature, $Mo_2Cl_2(NMe_3)_4$ (0.749 g,
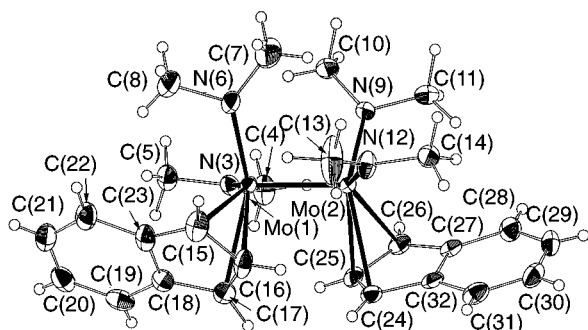
Fig. 1 An ORTEP drawing of the $Mo_2(C_9H_7)_2(NMe_2)_4$ molecule showing the atom number scheme. Thermal ellipsoids are drawn at the 40% probability level

Table 2 Selected bond distances (Å) and angles (°) for the $Mo_2(C_9H_7)_2(NMe_2)_4$ molecule

Mo(1)–Mo(2)	2.2516(5)	Mo(2)–N(9)	1.985(4)
Mo(1)–N(3)	1.963(3)	Mo(2)–N(12)	1.972(4)
Mo(1)–N(6)	1.975(4)	Mo(2)–C(24)	2.455(4)
Mo(1)–C(15)	2.549(5)	Mo(2)–C(25)	2.357(4)
Mo(1)–C(16)	2.374(5)	Mo(2)–C(26)	2.521(4)
Mo(1)–C(17)	2.462(5)		
Mo(2)–Mo(1)–N(3)	102.4(1)	Mo(1)–Mo(2)–N(9)	101.7(1)
Mo(2)–Mo(1)–N(6)	101.5(1)	Mo(1)–Mo(2)–N(12)	102.5(1)
Mo(2)–Mo(1)–C(15)	117.1(1)	Mo(1)–Mo(2)–C(24)	102.4(1)
Mo(2)–Mo(1)–C(16)	93.0(1)	Mo(1)–Mo(2)–C(25)	92.5(1)
Mo(2)–Mo(1)–C(17)	102.8(1)	Mo(1)–Mo(2)–C(26)	117.5(1)
N(3)–Mo(1)–N(6)	106.5(2)	N(9)–Mo(2)–N(12)	106.5(2)
N(3)–Mo(1)–C(15)	134.5(2)	N(9)–Mo(2)–C(24)	140.8(2)
N(3)–Mo(1)–C(16)	131.2(2)	N(9)–Mo(2)–C(25)	114.4(2)
N(3)–Mo(1)–C(17)	97.2(2)	N(9)–Mo(2)–C(26)	86.8(2)
N(6)–Mo(1)–C(15)	87.8(2)	N(12)–Mo(2)–C(24)	98.0(2)
N(6)–Mo(1)–C(16)	115.4(2)	N(12)–Mo(2)–C(25)	132.1(2)
N(6)–Mo(1)–C(17)	141.3(2)	N(12)–Mo(2)–C(26)	134.5(2)

1.71 mmol) was added in small amounts from a solids addition tube (1 h addition time). The reaction mixture was stirred for a further 14 h. Toluene was removed *in vacuo*. The residue was extracted with 10 cm^3 amounts of hexane until the extracts were virtually colourless. Hexane was removed *in vacuo* to yield a yellow-orange solid which was recrystallized from toluene at $-20\,°C$ (yield of yellow-orange crystals, 0.44 g, 52% based on tungsten) [Found: C, 42.72; H, 6.44; N, 10.66. Calc. for $C_{18}H_{34}Mo_2N_4$ (498.3): C, 43.48; H, 6.88; N, 11.24%]. IR (Nujol mull between CsI plates)/cm^{-1}: 2930ms, 2880ms, 2818m, 2770m, 1450ms, 1427ms, 1240ms, 1148s, 1127m, 1045ms, 1015ms, 950vs (br), 808 (sh), 797vs, 792s, 560vs, 391 (sh), 367vs, 320ms. ^1H NMR (C_6D_6 at 23 °C at 300 MHz, *gauche* rotamer): δ 6.24 [s, 10 H, C_5H_5], 4.15 [s, 12 H, $N(CH_3)_2$], 2.51 [s, 12 H, $N(CH_3)_2$].

Crystallographic studies

General operating procedures and listings of programs have been described.[15] A summary of crystal data for structural determinations reported here is given in Table 1.

$Mo_2(C_9H_7)_2(NMe_2)_4$. All hydrogen atoms were clearly visible in the Fourier-difference synthesis phased on the non-hydrogen parameters. All hydrogen atoms were refined isotropically and non-hydrogen atoms anisotropically in the final cycles. No absorption correction was performed. A final Fourier-difference map was featureless, with the largest peak being 0.48 e Å^{-3}.

$W_2(C_5H_4Me)_2(NMe_2)_4\cdot0.5C_6H_5Me$. Only a few of the hydrogen atoms were located in a Fourier-difference map. The

asymmetric unit contained one molecule of the W_2 complex as well as one half molecule of toluene solvent located at a center of symmetry. The hydrogen atoms were refined isotropically as were the toluene carbon atoms; all other atoms were refined anisotropically. The final difference map contained several peaks of about 2 e Å^{-3} in the immediate vicinity of the W atoms.

$W_2[(C_5H_4)_2SiMe_2](NMe_2)_4$. An orange crystal was examined but diffracted poorly. The cell parameters at $-169\,°C$ were $a = 17.1069(4)$, $b = 31.7519(8)$, $c = 8.7154(2)$ Å with space group *Pbca*. The poor quality of the diffraction data may have been the result of crystal twinning. Attempts to solve the structure revealed that while parts of the $(C_5H_4)_2Si$ and NMe_2 skeleton behaved well there were disorder problems which included the location of the W_2 unit.

CCDC reference number 186/586.

Results and Discussion

Synthesis

The new compounds reported in this work were prepared by metathetic reactions involving $1,2-M_2Cl_2(NMe_2)_4$ compounds and the sodium or lithium salts of cyclopentadienyl, methyl-cyclopentadienyl, indenyl and bis(methyl)bis(cyclopentadienyl)-silicon anions in thf or diethyl ether solvent. After the reaction was complete the solvent was removed and the residue extracted with CH_2Cl_2 or a hydrocarbon solvent. The salts, NaCl or LiCl, were removed by filtration and the orange filtrates were collected. The compounds of formula $1,2-Mo_2R_2(NMe_2)_4$, where $R = C_5H_4Me$ and indenyl, were then recrystallized. Typically these were yellow or orange, air-sensitive crystalline solids which were appreciably soluble in hydrocarbon solvents.

Solid-state and molecular structures

$1,2-Mo_2(C_9H_7)_2(NMe_2)_4$. An ORTEP[16] drawing of the molecular structure of the indenyl complex is given in Fig. 1 and a listing of selected bond distances and angles is given in Table 2.

The metrical parameters are very similar to those previously reported for the related $W_2(C_9H_7)_2(NMe_2)_4$ compound.[13] In particular, the Mo_2N_4 core is as expected for a *gauche* $M_2R_2(NMe_2)_4$ compound and the indenyl ligand is unequivocally η^3 bonded. Note the shortest Mo–C distances, 2.35 Å, are too long for a $Mo-C_{sp^2}$ bond distance, *cf.* Mo–C 2.16(1) Å in $Mo_2(p-C_6H_4Me)_2(NMe_2)_4$[12] and the longer distances 2.45–2.55 Å are well within π-bonding range. The other Mo–C distances to the C atoms that are common to both the C_5 and the C_6 rings are 2.80–2.88 Å, too long to be viewed as significant.

$W_2(C_5H_4Me)_2(NMe_2)_4$. An ORTEP drawing of the molecule is given in Fig. 2 and selected bond distances and angles are given in Table 3. The *gauche* nature of the W_2N_4 moiety is readily apparent and the striking feature with respect to the C_5H_4Me ligand is that the η^3 mode of co-ordination is as for the indenyl ligand. That is to say the W–C distances to the C_5H_4Me ligand are as they are in the indenyl complex. Thus, the well known indenyl-effect of ring slippage[17] is not the cause of the η^3-indenyl bonding in the $M_2(\eta^3-C_9H_7)_2(NMe_2)_4$ complexes. For $W_2(C_5H_4Me)_2(NMe_2)_4$, the four long $W\cdots C$ distances to the C_5 rings range from 2.71 to 2.80 Å. A view looking down the W–W bond is given in Fig. 3 which reveals how the Me groups of the C_5H_4Me ligands are disposed in a distal manner with respect to the W–W bond. The NC_2 blades are aligned along the M–M axis which favors Me_2N p_π to W d_π bonding and the W–N distances, 1.96(2) Å (average), are consistent with the view that there is supplemental W–N π bonding.[18] The view in Fig. 3 clearly reveals the virtual C_2 symmetry of the molecule.
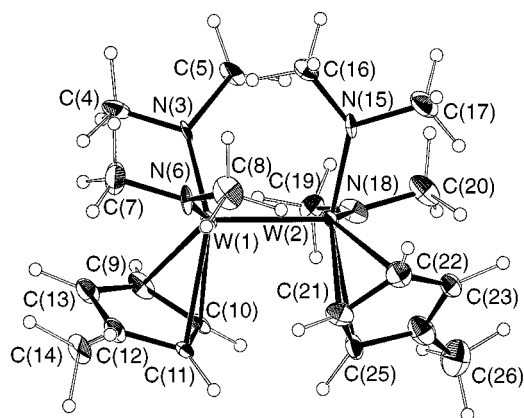
Fig. 2 An ORTEP drawing of the $W_2(C_5H_4Me)_2(NMe_2)_4$ molecule giving the atom number scheme used in Table 3. Thermal ellipsoids are drawn at the 40% probability level

Table 3 Selected bond distances (Å) and angles (°) for the W_2-$(C_5H_4Me)_2(NMe_2)_4$ molecule

W(1)–W(2)	2.345(1)	C(9)–C(13)	1.42(2)
W(1)–N(3)	1.96(1)	C(10)–C(11)	1.44(2)
W(1)–N(6)	1.99(1)	C(11)–C(12)	1.42(2)
W(1)–C(9)	2.51(1)	C(12)–C(13)	1.41(2)
W(1)–C(10)	2.36(1)	C(12)–C(14)	1.50(2)
W(1)–C(11)	2.47(2)	C(21)–C(22)	1.40(2)
W(2)–N(15)	1.96(1)	C(21)–C(25)	1.43(2)
W(2)–N(18)	1.97(1)	C(22)–C(23)	1.43(2)
W(2)–C(21)	2.38(2)	C(23)–C(24)	1.41(2)
W(2)–C(22)	2.53(2)	C(24)–C(25)	1.39(2)
W(2)–C(25)	2.44(2)	C(24)–C(26)	1.48(2)
C(9)–C(10)	1.40(2)		
W(2)–W(1)–N(3)	102.5(4)	N(6)–W(1)–C(9)	131.2(5)
W(2)–W(1)–N(6)	102.2(4)	N(6)–W(1)–C(10)	132.7(5)
W(2)–W(1)–C(9)	121.0(4)	N(6)–W(2)–N(15)	101.7(4)
W(2)–W(1)–C(10)	94.1(4)	W(1)–W(2)–N(15)	101.7(4)
N(3)–W(1)–N(6)	105.5(6)	W(1)–W(2)–N(18)	102.9(4)
N(3)–W(1)–C(9)	87.4(5)	W(1)–W(2)–C(21)	93.9(4)
N(3)–W(1)–C(10)	113.8(6)	W(1)–W(2)–C(22)	121.0(4)
N(3)–W(1)–C(11)	141.8(5)	W(1)–W(2)–C(25)	100.4(4)

$W_2[(C_5H_4)_2SiMe_2](NMe_2)_4$. Despite numerous attempts to grow crystals from various solvents we were not able to obtain suitable crystals for a complete structural determination. We were able to collect a data set but the quality of data was poor, quite possibly because of a twinning problem. A solution was attempted and a partial molecular structure was obtained. This revealed a disorder problem which involved not only the ligands but also the two tungsten atoms which were disordered over two positions, *i.e.* four positions at *ca.* 50% W occupancy. This type of disorder has been frequently encountered for $M_2X_8^{n-}$ ions where the X_8 unit forms a cube and the M_2 unit is disordered over three positions.[19] In the structure of $W_2(OSi-Me_2Bu^t)_6$ the O_6 unit forms an octahedron and the W_2 unit is disordered over three of the four possible orientations.[20] In the present case we were not able to model the disorder successfully but we were able to confirm the basic nature of the molecule. There is a $Me_2Si(C_5H_4)_2$ moiety that spans a W–W triple bond. The tetrahedral-like geometry at Si and the longer Si–C (Cp) distances, 1.8 Å, generate a C···C distance between the tips of the C_5H_4 ligands of 3.09 Å. This *gauche* C–W–W–C arrangement is similar to that in $W_2(C_5H_4-Me)_2(NMe_2)_4$ where the C(11) to C(25) distance is 3.21 Å. Suffice it to state that the two C_5 rings are not bonded to the same W atom but do indeed straddle the W–W triple bond to create a *gauche* $W_2C_2N_4$ moiety for which, in all likelihood, the C_5 rings are η^3-bonded.
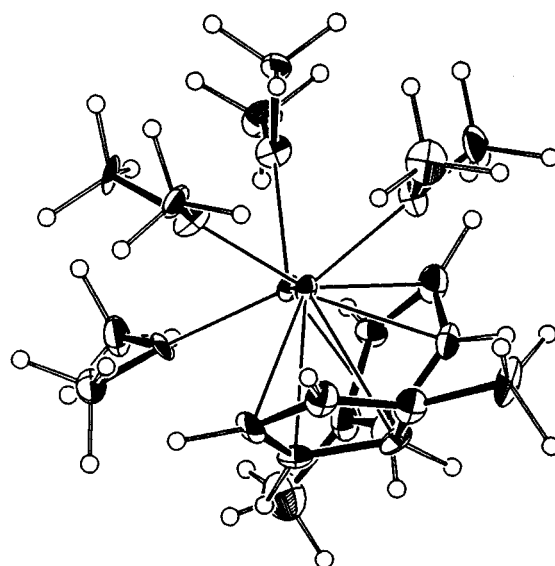

Fig. 3 View of the $W_2(C_5H_4Me)_2(NMe_2)_4$ molecule looking down the W–W axis

Other characterization data

Elemental analyses, infrared and NMR characterization data are given in the Experimental section. Of singular importance are the NMR data in the elucidation of the solution behavior of the present series of complexes.

All of the complexes show temperature-dependent NMR spectra as a result of rotations about M–NMe_2 bonds having $\Delta G^{\ddagger} \approx 10$–13 kcal mol^{-1} (cal = 4.184 J). At high temperatures (>80 °C in [$^2H_8$]toluene) two NMe_2 singlets are present due to the *gauche* nature of the $M_2R_2(NMe_2)_4$ molecules. At this temperature and above rotation about the M–N bonds is rapid. On cooling one resonance initially broadens and collapses into the base line. With further cooling the other resonance broadens while new resonances assignable to proximal and distal NMe groups separated by *ca.* 2 ppm appear. At −60 °C and below two sets of proximal and distal resonances are present, each of equal intensity. This confirms the presence of only the *gauche* rotamers; no *anti* rotamer is present to the limits of detection by NMR spectroscopy. An inspection of the observed structures for the indenyl and C_5H_4Me structures suggests that the *gauche* rotamer is favored on steric grounds as indeed it is for other 1,2-$M_2R_2(NMe_2)_4$ complexes where R = CH_2CMe_3 or CH-$(SiMe_3)_2$.[21] The indenyl complexes show inequivalent ring protons as do the C_5H_4Me ligands consistent with virtual C_2 symmetry. In the case of C_5H_5 ligands, even with C_2 symmetry, there is only a single CH resonance due to ring whizzing§[22] which is not frozen-out on the NMR time-scale even at −80 °C in [$^2H_8$]toluene.

Conclusion

The present work, coupled with earlier work, unequivocally establishes that the Cp ligand when bound to the $M_2(NMe_2)_4$ template co-ordinates in a η^3-mode. It is therefore competitive with the Me_2N ligands in terms of $\sigma^2\pi^2$ donation. The η^5-mode of co-ordination which is common for Cp ligands is presumably not favored because in this mode the η^5-Cp$^-$ ligand is a $\sigma^2\pi^4$ donor. This would disrupt the W≡W and Me_2N–W π bonding and could only occur with an alternate geometry. In this regard we note that the η^5-C_5 mode of co-ordination was seen in the structure of $W_2Cp_2(NMe_2)(O_2CEt)_3$ which has bridging NMe_2 and O_2CEt ligands.[13] Also in Cp'$_2W_2Cl_4$, where Cp' = C_5H_4Pr,[23]

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§ The first recognition of a fluxional organometallic molecule was in (η^5-C_5H_5)Fe(CO)$_2$(η^1-C_5H_5) and Hg(C_5H_5)$_2$.

the η^5-C_5 co-ordination is approximated because the Cl ligands are not, relative to Me_2N ligands, strong π donors.

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