Registry No. $Cp_2ZrH(Cl)$, 37342-97-5; BCl_3, 10294-34-5; BBr_3, 10294-33-4; $B(OMe)_3$, 121-43-7; *B*-bromo-9-BBN, 22086-45-9; *B*-methoxy-9-BBN, 38050-71-4; *B*-(*E*)-1-hexenyl-9-BBN pyridine complex, 136115-27-0; *B*-(*E*)-1-hexenyl-9-BBN, 69322-45-8; 1-hexyne, 693-02-7; bis(cyclopentadienyl)-1-hexenylzirconium chloride, 79083-22-0; bis(cyclopentadienyl)-1-octenylzirconium chloride, 63175-90-6; *B*-chlorocatecholborane, 55718-76-8; *B*-bromocatecholborane, 51901-85-0; *B*-chloro-1,3,2-dioxaborinane, 1003-43-6; *B*-chlorodiisopropoxyborane, 66009-09-4; dicyclohexylchloroborane, 36140-19-9; *B*-chlorohexylhexylborane, 88817-20-3; *B*-chlorodiisopinocamphenylborane, 85116-37-6; (*E*)-1-hexenyldichloroborane, 51207-21-7; (*E*)-1-hexenyldibromoborane, 72228-55-8; *B*-(*E*)-1-hexenyl-1,3,2-benzodioxaborole, 37490-22-5; *B*-(*E*)-1-hexenyl-1,3,2-dioxaborinane, 91083-28-2; (*E*)-1-hexenyldiisopropoxyborane, 91083-27-1; (*E*)-1-hexenyldicyclohexylborane, 37609-12-4; thexylhexyl-(*E*)-1-hexenylborane, 136089-08-2; *B*-(*E*)-1-hexenyldiisopinocamphenylborane, 70179-28-1; (*E*)-1-hexenyldimethoxyborane, 91083-26-0; 1-bromo-1-hexyne, 1119-64-8; dibromoborane–methyl sulfide, 55671-55-1; (1-bromo-1-hexenyl)dibromoborane, 136089-09-3; (1-bromo-1-hexenyl)-1-octenylbromoborane, 136089-10-6; isobutyric acid, 79-31-2; *trans,trans*-5,7-tetradecadiene, 73349-16-3.

Synthesis of Cadmium Pentamethylcyclopentadienyl Complexes

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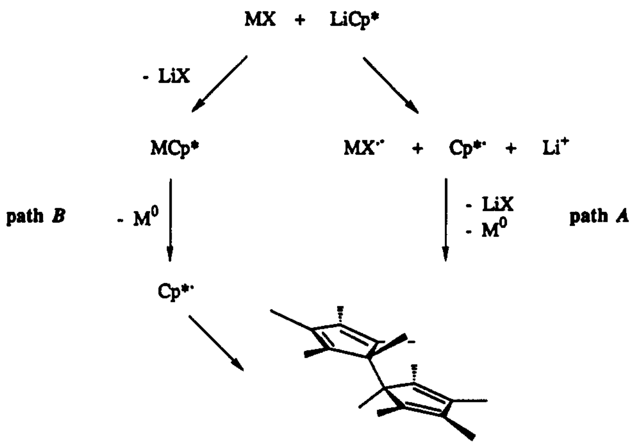
Summary: The preparation of red, light-sensitive cadmium bis(pentamethylcyclopentadienide) has been effected by reaction of $Cd(acac)_2$ with 2 equiv of LiCp* in the dark. $CdCp^*_2$ forms a weak adduct with 1,2-dimethoxyethane (DME). A Schlenk-type equilibrium exists when $CdCp^*_2$ is mixed with an equimolar amount of $Cd[N(SiMe_3)_2]_2$, giving solutions from which $(CdCp^*[N(SiMe_3)_2])_2$ can be crystallized. Single-crystal X-ray diffraction revealed the dimeric nature of the latter complex, which displays bridging silylamides and terminal Cp* ligands. Bonding of the Cp* ligand to cadmium in this complex is regarded primarily as σ in character, but a weak dative interaction between the diene HOMO and the empty cadmium p_z orbital is plausible in view of structural parameters. The structure determination is believed to be the first on any complex containing either a cadmium amide *or* a cadmium pentamethylcyclopentadienide linkage.

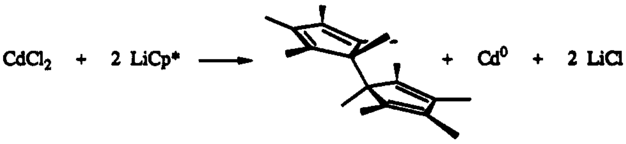
Introduction

Cadmium compounds that contain bulky ligands are currently of interest with respect to the design of molecular precursors to semiconductors such as CdS and CdSe.[1] Alkyl,[1a] thiophenoxide,[1b] and selenophenoxide[1b] complexes are examples that recently have been synthesized with this purpose in mind. The absence of pentamethylcyclopentadienyl (Cp*) complexes in the list is especially surprising, since the Cp* ligand has been useful in stabilizing a wide variety of low-coordinate compounds that contain metals throughout the periodic table.[2] We became interested in preparing Cp* cadmium complexes as part of a project concerned with the synthesis of semiconductor clusters employing ROMP block copolymer technology.[3]

Scheme I



It is reported in the literature that $CdCl_2$ is efficiently reduced by LiCp* in tetrahydrofuran (THF) to give colloidal cadmium, LiCl, and $C_{10}Me_{10}$ (eq 1).[4] Although



(1)

details of this reaction are not known, $C_{10}Me_{10}$ most likely is formed via coupling of C_5Me_5 radicals, which are known to be generated upon oxidation of $C_5Me_5^-$ or upon photolysis of Cp* derivatives (including the parent hydrocarbon, C_5Me_5H) and to combine to give $C_{10}Me_{10}$ at diffusion-controlled rates.[5] Interestingly, Jutzi and Kohl expressed doubt that the original report[6] of $HgCp^*_2$ is correct, since its reported ^1H NMR spectrum is virtually identical with that obtained by them for $C_{10}Me_{10}$, which they produced by adding pyridine to $SnCp^*_2I_2$.[7] It also

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[1] (a) Bauch, C. G.; Johnson, C. E. *Inorg. Chim. Acta* **1989**, *164*, 165. (b) Bochmann, M.; Webb, K.; Harman, M.; Hursthouse, M. B. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 638.

[2] Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA , 1987.

[3] (a) Sankaran, V.; Cummins, C. C.; Schrock, R. R.; Cohen, R. E.; Silbey, R. J. *J. Am. Chem. Soc.* **1990**, *112*, 6858. (b) Cummins, C. C.; Beachy, M. D.; Schrock, R. R.; Vale, M. G.; Sankaran, V.; Cohen, R. E. Submitted for publication.

[4] Blom, R. *Acta Chem. Scand.* **1988**, *A42*, 445. This reference describes the gas-phase structure of $C_{10}Me_{10}$; for the crystalline structure of the hydrocarbon see: Lorberth, J.; et al. *Abstracts of the XIIIth ICOC*; Turin, Italy, 1988.

[5] Davies, A. G.; Lusztyk, J. *J. Chem. Soc., Perkin Trans. 2* **1981**, 692.

[6] Floris, B.; Illuminati, G.; Ortaggi, G. *J. Chem. Soc., Chem. Commun.* **1969**, 492.

[7] Jutzi, P.; Kohl, F. *J. Organomet. Chem.* **1979**, *164*, 141.

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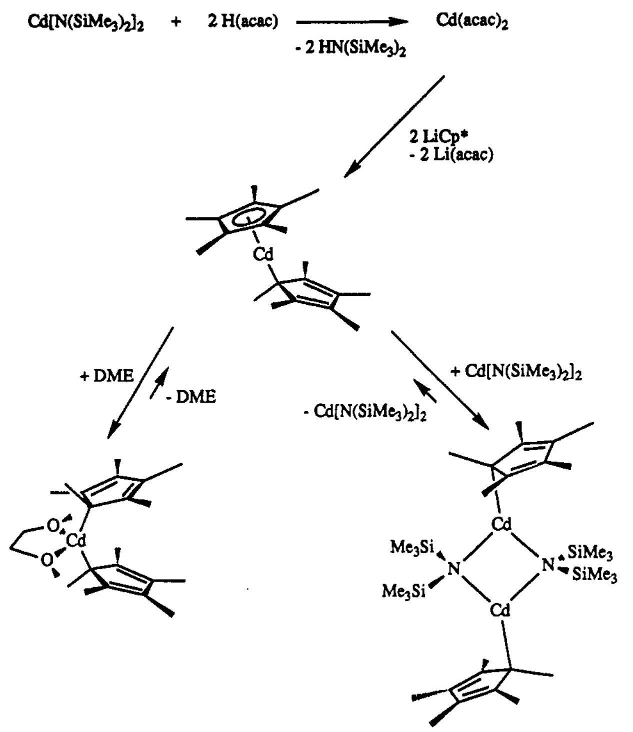
Scheme II



has been reported that $C_{10}Me_{10}$ is formed as a byproduct of the preparation of TlCp*.[8a] The hydrocarbon has similarly been produced in the chemistry of antimony,[8b] copper,[8c] and platinum.[8d] Pentamethylcyclopentadienyl radicals could form either by electron transfer from $C_5Me_5^-$ to the main-group metal compound without metal–carbon bound formation (Scheme I, path *A*) or by homolytic fission of a metal–carbon bond (Scheme I, path *B*). We speculated that C_5Me_5 radicals in the reaction involving $CdCl_2$ are formed faster via path *A*, and therefore that employing a less electrophilic cadmium complex such as $Cd(acac)_2$ would decrease the likelihood of electron transfer.[9] In this paper we report the results of experiments based on this premise.

Results and Discussion

Slow addition of $Cd(acac)_2$ powder to a stirred slurry of LiCp* in THF in the absence of light yields a homogeneous reaction mixture containing a small amount of black insoluble material, which we presume to be cadmium metal. Pentane-soluble, waxy, orange-red $CdCp^*_2$ can be isolated from this mixture in good yield (Scheme II). At this stage it contains only trace quantities of $C_{10}Me_{10}$ (>95% pure by proton NMR analysis). Further purification is possible by sublimation (55 °C, 0.05 Torr), but the crude product is adequate for further reactions. Manipulations involving solutions of $CdCp^*_2$ were performed in the dark, as 30 min exposure to normal fluorescent laboratory light was sufficient to cause complete decomposition to $C_{10}Me_{10}$ and Cd^0.

The solubility of $CdCp^*_2$ in pentane contrasts sharply with the insoluble and presumably polymeric nature of $CdCp_2$[10] and suggests that $CdCp^*_2$ is likely to be monomeric. Unfortunately, we were not able to obtain an X-ray structure, since $CdCp^*_2$ could not be induced to crystallize, even from highly concentrated solutions (THF, diethyl ether, toluene, pentane, or $SiMe_4$) at −40 °C. The fact that the color of hydrocarbon solutions of $CdCp^*_2$ are a rich orange-red, while the color of THF or diethyl ether solutions tends to orange suggests that donor solvents may coordinate to cadmium. Indeed, a yellow solution is generated when $CdCp^*_2$ is dissolved in 1,2-dimethoxyethane (DME) and cooling a red pentane solution containing $CdCp^*_2$ along with 1 equiv of DME to −40 °C yields a yellow solution from which yellow, crystalline $CdCp^*_2$(DME) can be obtained in high yield (Scheme II). Dimethoxyethane must be only weakly bound in $CdCp^*_2$(DME). It redissolves in pentane to give a red solution characteristic of $CdCp^*_2$, and if a toluene solution of $CdCp^*_2$(DME) is reduced to dryness in vacuo $CdCp^*_2$ is regenerated quantitatively. Crystals of $CdCp^*_2$(DME) melt upon warming to room temperature.

The precise structure of $CdCp^*_2$ is a matter of speculation. An η^1,η^5 arrangement of the Cp* ligands is perhaps the most likely closed-shell configuration, since that is the structure of $ZnCp^*_2$ as determined by gas-phase electron diffraction.[11] Other possibilities that cannot be discounted include the η^3,η^3 arrangement and the η^1,η^1 arrangement. The latter is not a closed-shell configuration, but on the other hand Cd and Hg exhibit less tendency to engage in π-bonding than Zn, and formally 14-e species such as $CdMe_2$, of course, are relatively stable as base-free monomers. DME is likely bound in an η^2 fashion in $Cd(\eta^1\text{-}C_5Me_5)_2$(DME) (Scheme II) to give a closed-shell configuration. An IR spectrum of $CdCp^*_2$ reveals two ring C=C stretching modes at 1670 and 1570 cm^{-1} (neat film), consistent with an η^1,η^5 arrangement of the Cp* ligands.[12]

Only a singlet resonance at 1.89 ppm is found in the proton NMR spectrum of $CdCp^*_2$ at room temperature, consistent with fluxional behavior of the Cp* ligands, behavior that is widespread among main-group cyclopentadienyl complexes.[13] ($ZnCp^*_2$ also exhibits a singlet resonance,[11b] as does $CdCp_2$ (in pyridine-d_5).[10]) The absence of coupling of the methyl protons to ^{113}Cd ($I = {}^1/_2$, 12.3% abundance) suggests that rings exchange rapidly between cadmium centers on the NMR time scale.[14] Coupling to cadmium is observed in a Cp* complex, discussed below, and for $CdMe_2$, a compound in which alkyl exchange is fast on the chemical time scale.[14]

A crystalline Cp* derivative was sought in order to obtain more structural information. Mixing $CdCp^*_2$ with an equimolar amount of $Cd[N(SiMe_3)_2]_2$[15] yielded an orange solution (in pentane or benzene), a proton NMR spectrum of which in C_6D_6 reflected the presence of $CdCp^*_2$ (~12%), $Cd[N(SiMe_3)_2]_2$ (~12%), and a new species formulated as $CdCp^*[N(SiMe_3)_2]$ (~76%) (Scheme II). The Cp* resonance in $CdCp^*[N(SiMe_3)_2]$ is found at δ 1.93 and is flanked by ^{113}Cd satellites (24 Hz), consistent with a

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[8] (a) Rupprecht, G. A.; Messerle, L. W.; Fellman, J. D.; Schrock, R. R. *J. Am. Chem. Soc.* **1980**, *102*, 6236. (b) Berlitz, T. F.; Sinning, H.: Lorberth, J.; Müller, U. *Z. Naturforsch.* **1988**, *B43*, 744. (c) Zybill, C.; Müller, G. *Organomet.* **1987**, *6*, 2489. (d) Boag, N. M.; Green, M. E.; Terill, N. *Abstracts of the XIIIth ICOC*; Turin, Italy, 1988.

[9] Acac derivatives have been used as precursors to transition-metal Cp* complexes. See for example: Bunel, E. E.; Valle, L.; Manriquez, J. M. *Organometallics* **1985**, *4*, 1680.

[10] Lorberth, J. *J. Organomet. Chem.* **1969**, *19*, 189.

[11] (a) Blom, R.; Haaland, A.; Weidlein, J. *J. Chem. Soc., Chem. Commun.* **1985**, 266. (b) Blom, R.; Boersma, J.; Budzelaar, P. H. M.; Fischer, B.; Haaland, A.; Volden, H. V.; Weidlein, J. *Acta Chem. Scand.* **1986**, *A40*, 113. For an X-ray crystallographic determination of the structure of $ZnCp^*_2$, where the η^1,η^5 geometry is also displayed see: Fischer, B.; Wijkens, P.; Boersma, J.; van Koten, G.; Smeets, W. J. J.; Spek, A. L.; Budzelaar, P. H. M. *J. Organomet. Chem.* **1989**, *376*, 223.

[12] A C_5 ring mode at 1652 cm^{-1} was observed for $ZnCp^*_2$ (see ref 11b; a partial IR spectrum was reported) and assigned to an η^1-bonded ring with localized single and double bonds.

[13] Davison, A.; Rakita, P. E. *Inorg. Chem.* **1970**, *9*, 289.

[14] Cardin, A. D.; Ellis, P. D.; Odom, J. D.; Howard, J. W., Jr. *J. Am. Chem. Soc.* **1975**, *97*, 1672.

[15] Bürger, H.; Sawodny, W.; Wannagat, U. *J. Organomet. Chem.* **1965**, *3*, 113.

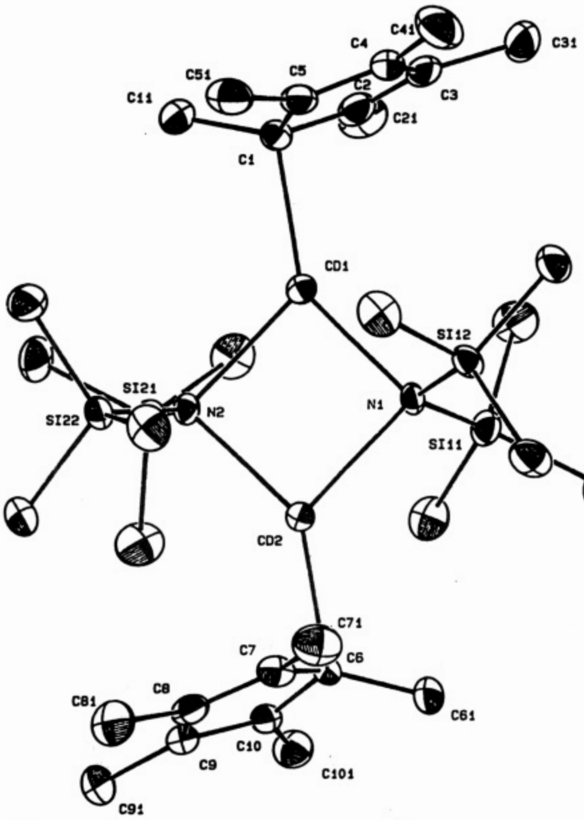

Figure 1. ORTEP drawing of (CdCp*[N(SiMe$_3$)$_2$])$_2$ (35% probability ellipsoids; refer to Table I for bond distances and angles).

Table I. Selected Distances (Å) and Angles (deg) for (CdCp*[N(SiMe$_3$)$_2$])$_2$[a]

Cd(1)–N(1)	2.257 (5)	C(8)–C(9)	1.447 (9)
Cd(1)–N(2)	2.338 (5)	C(9)–C(10)	1.365 (8)
Cd(1)–C(1)	2.220 (6)	C(10)–C(6)	1.458 (8)
Cd(1)–Cd(2)	3.2279 (6)	N(1)–Cd(1)–N(2)	90.2 (2)
Cd(1)–C(2)	2.881 (7)	C(1)–Cd(1)–N(1)	143.7 (2)
Cd(1)–C(5)	2.839 (6)	C(1)–Cd(1)–N(2)	126.0 (2)
Cd(2)–N(1)	2.323 (5)	N(1)–Cd(2)–N(2)	90.7 (2)
Cd(2)–N(2)	2.254 (4)	C(6)–Cd(2)–N(1)	125.4 (2)
Cd(2)–C(6)	2.224 (6)	C(6)–Cd(2)–N(2)	143.9 (2)
Cd(2)–C(7)	2.793 (6)	Cd(1)–N(1)–Cd(2)	89.6 (2)
Cd(2)–C(10)	2.890 (6)	Cd(1)–N(2)–Cd(2)	89.3 (2)
C(1)–C(2)	1.453 (9)	Cd(1)–C(1)–C(11)	112.2 (4)
C(2)–C(3)	1.38 (1)	Cd(1)–C(1)–C(2)	101.3 (4)
C(3)–C(4)	1.437 (9)	Cd(1)–C(1)–C(5)	97.8 (4)
C(4)–C(5)	1.372 (9)	Cd(2)–C(6)–C(61)	112.8 (4)
C(5)–C(1)	1.495 (9)	Cd(2)–C(6)–C(7)	96.3 (4)
C(6)–C(7)	1.461 (8)	Cd(2)–C(6)–C(10)	101.3 (4)
C(7)–C(8)	1.354 (9)		

[a] Atoms are labeled as shown in Figure 1.

slower intermolecular exchange relative to that in CdCp*$_2$. Cooling a similar mixture in pentane to −40 °C yields yellow crystals (84% yield) whose elemental analysis is consistent with the formulation CdCp*[N(SiMe$_3$)$_2$]. Since neither CdCp*$_2$ nor Cd[N(SiMe$_3$)$_2$]$_2$ is crystalline (the latter is liquid at room temperature), the yellow crystals most likely consist solely of CdCp*[N(SiMe$_3$)$_2$]. Crystalline CdCp*[N(SiMe$_3$)$_2$] dissolves in benzene to give an orange solution whose proton NMR spectrum is identical with that obtained for a mixture of CdCp*$_2$ and Cd[N(SiMe$_3$)$_2$]$_2$, indicating that the three engage in a Schlenk-type equilibrium at room temperature.[16a] A related preparation of HgCp[N(SiMe$_3$)$_2$] has been reported.[16b]

Table II. Atomic Coordinates and Thermal Parameters (Å^2) for (CdCp*[N(SiMe$_3$)$_2$])$_2$

atom	x	y	z	B(eq)
Cd(1)	0.18675 (3)	0.06974 (3)	0.24371 (2)	2.16 (2)
Cd(2)	0.33257 (2)	−0.07221 (3)	0.26679 (2)	2.10 (2)
Si(11)	0.2716 (1)	0.0208 (1)	0.4381 (1)	2.87 (8)
Si(12)	0.1398 (1)	−0.0899 (1)	0.3543 (1)	2.63 (8)
Si(21)	0.3664 (1)	0.1138 (1)	0.1729 (1)	2.83 (8)
Si(22)	0.2847 (1)	−0.0259 (1)	0.0714 (1)	2.72 (8)
N(1)	0.2269 (3)	−0.0217 (3)	0.3461 (3)	2.2 (2)
N(2)	0.2986 (3)	0.0251 (3)	0.1679 (3)	2.1 (2)
C(1)	0.0937 (4)	0.1697 (4)	0.2061 (4)	2.6 (3)
C(2)	0.0802 (4)	0.2101 (4)	0.2849 (4)	3.4 (3)
C(3)	0.0102 (5)	0.1745 (5)	0.3168 (4)	3.6 (3)
C(4)	−0.0268 (4)	0.1144 (5)	0.2585 (4)	3.4 (3)
C(5)	0.0200 (4)	0.1121 (4)	0.1904 (4)	3.0 (3)
C(6)	0.4205 (4)	−0.1778 (4)	0.3022 (4)	2.4 (3)
C(7)	0.3947 (4)	−0.2350 (4)	0.2342 (4)	2.9 (3)
C(8)	0.4504 (4)	−0.2279 (4)	0.1749 (4)	3.0 (3)
C(9)	0.5166 (4)	−0.1697 (4)	0.2021 (4)	2.8 (3)
C(10)	0.4998 (4)	−0.1419 (4)	0.2791 (4)	2.6 (3)
C(11)	0.1225 (4)	0.2250 (5)	0.1351 (4)	3.6 (3)
C(21)	0.1305 (5)	0.2827 (5)	0.3224 (5)	4.7 (4)
C(31)	−0.0233 (6)	0.1940 (5)	0.3999 (5)	5.8 (5)
C(41)	−0.1035 (5)	0.0632 (6)	0.2702 (6)	5.4 (4)
C(51)	0.0001 (4)	0.0673 (5)	0.1103 (4)	4.4 (4)
C(61)	0.4137 (4)	−0.2066 (5)	0.3906 (4)	3.9 (3)
C(71)	0.3243 (5)	−0.2981 (5)	0.2366 (5)	4.7 (4)
C(81)	0.4475 (5)	−0.2745 (5)	0.0931 (4)	5.0 (4)
C(91)	0.5891 (4)	−0.1473 (5)	0.1531 (4)	4.1 (4)
C(101)	0.5583 (4)	−0.0892 (5)	0.3348 (4)	3.6 (3)
C(111)	0.3849 (4)	0.0434 (5)	0.4289 (4)	3.8 (3)
C(112)	0.2200 (5)	0.1229 (5)	0.4668 (4)	4.4 (4)
C(113)	0.2689 (5)	−0.0519 (5)	0.5293 (4)	4.7 (4)
C(121)	0.1651 (4)	−0.1969 (4)	0.4009 (5)	4.0 (4)
C(122)	0.0587 (4)	−0.0391 (5)	0.4147 (5)	3.8 (3)
C(123)	0.0915 (4)	−0.1114 (5)	0.2501 (5)	4.1 (4)
C(211)	0.3643 (5)	0.1823 (5)	0.0793 (4)	4.4 (4)
C(212)	0.4760 (4)	0.0810 (5)	0.1963 (5)	4.9 (4)
C(213)	0.3361 (5)	0.1883 (4)	0.2546 (4)	3.9 (3)
C(221)	0.2305 (5)	−0.1298 (5)	0.0796 (4)	4.3 (4)
C(222)	0.2210 (4)	0.0376 (5)	−0.0067 (4)	4.4 (4)
C(223)	0.3869 (4)	−0.0499 (5)	0.0281 (4)	4.1 (4)

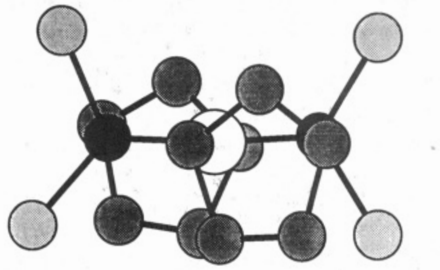

Figure 2. View of (CdCp*[N(SiMe$_3$)$_2$])$_2$ down the Cd(1)–Cd(2) vector (all methyl groups omitted for clarity).

An X-ray study reveals that CdCp*[N(SiMe$_3$)$_2$] is a dimer in the solid state with what at first sight is an η^1-C$_5$Me$_5$ ligand and bridging N(SiMe$_3$)$_2$ ligands (Figure 1; Tables I and II). Other instances of N(SiMe$_3$)$_2$ behaving as a bridging ligand in the crystalline phase have been observed; for example Li[N(SiMe$_3$)$_2$] is a cyclic trimer,[17a] while M[N(SiMe$_3$)$_2$]$_2$ (M = Mn, Co) are dimeric,[17b,c] displaying M$_2$N$_2$ rings as in the present case. The asymmetric Cd$_2$N$_2$ ring is nearly planar with a Cd(1)–N(1)/Cd(2)–N(2) average distance smaller (by 0.075 (5) Å) than the Cd(1)–N(2)/Cd(2)–N(1) average distance. The C$_2$ axis perpendicular to the Cd$_2$N$_2$ plane (Figure 2) is not crystallo-

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[16] (a) Evans, D. F.; Phillips, R. F. *J. Chem. Soc. Dalton Trans.* **1973**, 978. (b) Lorberth, J.; Sarraje, I. *J. Organomet. Chem.* **1978**, *146*, 113.

[17] (a) Mootz, D.; Zinnius, A.; Böttcher, B. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 378. (b) Bradley, D. C.; Hursthouse, M. B.; Malik, K. M. A.; Möseler, R. *Transition Met. Chem.* **1978**, *3*, 253. (c) Andersen, R. A.; Faegri, K., Jr.; Green, J. C.; Haaland, A.; Lappert, M. F.; Leung, W.-P.; Rypdal, K. *Inorg. Chem.* **1988**, *27*, 1782.

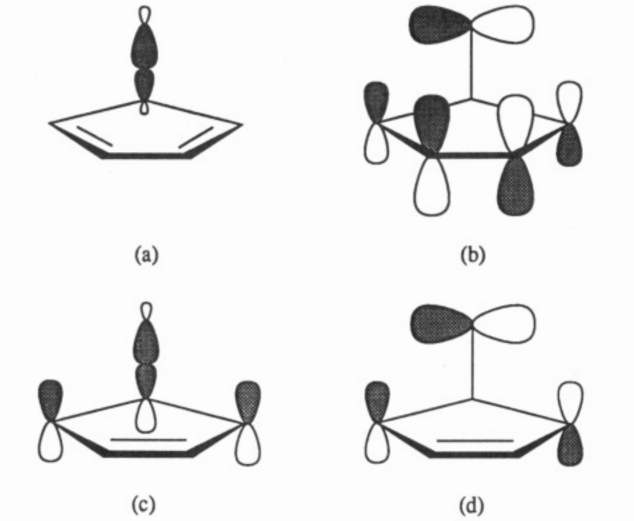

Figure 3. Descriptions of bonding between the cadmium and the cyclopentadienyl ring: (a) σ bond between the metal and an η^1-bound ring; (b) p_z orbital and diene HOMO; (c) σ bond between the metal and an η^3-bound ring; (d) π bond between the metal and an η^3-bound ring.

graphically imposed. The coordination geometry about the metals is a distorted trigonal plane with the sum of the angles at the metal being close to 360°. There is precedent for trigonal-planar cadmium complexes that contain bulky ligands.[1b,18]

A closer examination (Figure 2) reveals that the Cp* ligand is nearly bisected by the xy plane (taking the z axis as perpendicular to the trigonal plane), and C(1) and C(6) are not strictly tetrahedral; the angles Cd(1)–C(1)–C(2) and Cd(1)–C(1)–C(5), for example, average to 100°, with tilting of the diene fragment toward the metal. Localization of double bonds in the pentamethylcyclopentadienyl ring also is evident (C(4)–C(5) = 1.372 (9) Å and C(2)–C(3) = 1.38 (1) Å), and the Cd(1)–C(2) and Cd(1)–C(5) distances are long (respectively, 2.881 (7) and 2.839 (6) Å) compared to the Cd(1)–C(1) distance (2.220 (6) Å). Although the primary interaction between Cd and the ring is a simple σ bond (Figure 3a), it should be noted that the HOMO of the diene fragment is of the correct symmetry to bond with the available cadmium p_z orbital in a dative fashion (Figure 3b), an interaction that would draw the diene fragment toward the metal as observed. A bonding scheme with similar symmetry properties could be realized if the Cp* ligand were considered to bind as an allyl (Figure 3c,d). The two bonding schemes presented in Figure 3 are two extreme views of a continuum. An inability of the filled cadmium 4d subshell to engage in π-back-bonding yields a situation that in our opinion is best described by Figure 3a,b.

We believe the structure determination of (CdCp*[N(SiMe$_3$)$_2$])$_2$ to be the first of a cadmium compound that contains either a pentamethylcyclopentadienyl linakge *or* a cadmium amide linkage. Its structure should be compared with that of HgCp*Cl and ZnCp*$_2$. Polymeric HgCp*Cl consists of linear Cp*–Hg–Cl units associated by weak Hg–Cl bridge bonds;[19] the Cp* is strictly η^1, exhibiting angles between the ring plane and the Hg–C bond axis of 113 and 108°. Although the structure of ZnCp*$_2$, as determined by electron diffraction, shows the angle between the plane of the relevant cyclopentadienyl ligand and its Zn–C σ bond to be relatively acute (87 (3)[11a] or 84 (4)°[11b]), it was described as "more or less η^1". In this case bonding of the η^5-C$_5$Me$_5$ ligand would be expected to deprive the second Cp* ligand the possibility of bonding in an η^3 fashion.

Experimental Section

General Procedures. All experiments were performed under a nitrogen atmosphere in a Vacuum Atmospheres drybox or by using standard Schlenk techniques, unless otherwise stated. Reagent grade diethyl ether, tetrahydrofruan (THF), and toluene were distilled from purple sodium benzophenone ketyl under nitrogen. Pentane was washed with 5% nitric acid in sulfuric acid, stored over calcium chloride, and then distilled from purple sodium benzophenone ketyl under nitrogen. Deuterated benzene was vacuum-transferred from purple sodium benzophenone ketyl. Acetylacetone was dried over 4-Å molecular sieves and distilled. Cd[N(SiMe$_3$)$_2$]$_2$ was prepared as previously described.[15] ^{13}C and ^{1}H NMR data are listed in parts per million downfield from TMS; coupling constants are in hertz.

Preparation of Compounds. Cd(acac)$_2$. A solution of acetylacetone (4.329 g, 43.23 mmol, 2.1 equiv) in 8 mL of ether was added dropwise to a solution of Cd[N(SiMe$_3$)$_2$]$_2$ (8.918 g, 20.59 mmol) in 125 mL of ether. The reaction mixture was stirred for 1 h, and the white product was collected on a frit, washed with 50 mL of ether, and dried in vacuo; yield 5.88 g (92%).

CdCp*$_2$. Cd(acac)$_2$ (3.058 g, 9.85 mmol) was added to a slurry of LiCp* (2.800 g, 19.69 mmol) in 65 mL of THF over a period of 50 min in the dark. A small amount of gray-black solid (pyrophoric) was removed by filtration, and the filtrate was taken to dryness in vacuo. The residue was extracted with 60 mL of pentane, and the mixture was filtered to give an orange-red solution. Concentration of the solution in vacuo gave crude CdCp*$_2$ (2.891 g, 7.55 mmol, 77%) as an oily solid that was >95% pure by ^{1}H NMR spectroscopy. Sublimation of CdCp*$_2$ (303 mg, 0.05 Torr, 50 °C) onto a O °C probe in the dark gave pure CdCp*$_2$ in 58% yield: ^{1}H NMR (C$_6$D$_6$) δ 1.89; ^{13}C NMR (C$_6$D$_6$) δ 115.8 (CCH$_3$), 11.9 (CCH$_3$).

CdCp*$_2$(DME). CdCp*$_2$ (350 mg, 914 μmol) was added to a vial containing DME (3 mL) to give a yellow solution. Filtration of this solution and concentration of the filtrate is vacuo gave a yellow crystalline solid. The residue (still cold) was dissolved in pentane (3 mL). Cooling the solution to −40 °C produced a crop of yellow crystals from which the supernatant was decanted. The product was placed briefly under vacuum, after which the previously weighed vial was reweighed; yield 366 mg (91%). Crystals of CdCp*$_2$(DME) melt at room temperature. A melted sample was dissolved in toluene to give an orange solution that was concentrated in vacuo to give a waxy orange-red solid. Examination by ^{1}H NMR spectroscopy revealed the residue to be pure CdCp*$_2$ with no DME remaining.

(CdCp*[N(SiMe$_3$)$_2$])$_2$. A solution of CdCp*$_2$ (500 mg, 1.306 mmol) in 8 mL of pentane was treated with a solution of Cd[N(SiMe$_3$)$_2$]$_2$ (566 mg, 1.306 mmol) in 3 mL of pentane. The resulting yellow-orange solution was diluted with pentane (10 mL), filtered, and taken to dryness in vacuo to yield a yellow crystalline solid that was recrystallized from minimum pentane at −40 °C; yield 894 mg (84%): ^{1}H NMR (C$_6$D$_6$) δ 1.93 (s, 15, Cp*, J_{CdH} = 24), 0.11 (s, 18, N(SiMe$_3$)$_2$). Also present are CdCp*$_2$ (12.5%; δ 1.89) and Cd[N(SiMe$_3$)$_2$]$_2$ (12.5%; δ 0.18; ^{13}C NMR (C$_6$D$_6$) δ 116.5 (CCH$_3$, J_{CdC} = 46), 12.0 (CCH$_3$), 5.8 (N(Si(CH$_3$)$_3$)$_2$). Anal. Calcd for C$_{32}$H$_{66}$N$_2$Si$_4$Cd$_2$: C, 47.10; H, 8.15; N, 3.43. Found: C, 46.81; H, 8.50; N, 3.19.

X-ray Structure of (CdCp*[N(SiMe$_3$)$_2$])$_2$. A yellow crystal of approximate dimensions 0.18 × 0.18 × 0.15 mm was mounted on a glass fiber in a stream of cold N$_2$. Data were collected at −73 °C on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated Mo Kα radiation. A total of 9962 reflections were collected to a 2θ value of 55°, of which 9623 were unique (R_{int} = 0.040); equivalent reflections were merged. The structure was solved by a combination of Patterson and difference Fourier techniques. Non-hydrogen atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement was based on 5851 observed reflections ($I > 3.00\sigma(I)$) and 362 variable parameters and converged (largest parameter shift was less than

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0.009 times its esd) with $R = 0.048$ and $R_w = 0.050$. A final difference-Fourier map showed no chemically significant features. Crystal data are $a = 16.027$ (2) Å, $b = 15.622$ (1) Å, $c = 16.228$ (1) Å, $\beta = 93.269$ (8)°, $V = 4056$ (1) Å^3, space group $P2_1/a$, $Z = 4$, mol wt = 816.05, and ρ(calcd) = 1.336 g/cm^3.

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Supplementary Material Available: Tables of positional parameters and final thermal parameters for $(CdCp^*[N(SiMe_3)_2])_2$ (5 pages); a listing of final observed and calculated structure factors for $(CdCp^*[N(SiMe_3)_2])_2$ (63 pages). Ordering information is given on any current masthead page.

Synthesis of Two Novel Pentanuclear Rhodium Clusters Bearing the Alkyl-like Ligands CH_2COOMe and CH_2CN. X-ray Structure of $[PPh_4]_2[Rh_5(\mu\text{-}CO)_6(CO)_8(CH_2CN)]$

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Summary: The reaction of $[PPh_4][Rh(CO)_4]$ (**1**) under CO with $BrCH_2COOMe$ or $BrCH_2CN$ in a 5:3 molar ratio gave high yields of the two novel clusters $[PPh_4]_2[Rh_5(CO)_{14}(CH_2COOMe)]$ (**3a**) and $[PPh_4]_2[Rh_5(CO)_{14}(CH_2CN)]$ (**3b**), respectively, which appear to be the first examples of rhodium clusters bearing an alkyl-like ligand. The first step of the reaction is the rapid formation of $[PPh_4][RhBr(CO)_2(CH_2R)]$ (R = COOMe (**2a**), CN (**2b**)), which further react, much more slowly, with an excess of $[Rh(CO)_4]^-$ to yield the cluster compounds. **3a,b** are indefinitely stable in the solid state under CO atmosphere. Crystals of **3b** suitable for an X-ray diffraction study could be obtained. **3b** is monoclinic, space group $P2_1/c$ with $a = 12.488$ (3) Å, $b = 43.585$ (9) Å, $c = 23.222$ (8) Å, $\beta = 91.46$ (4)°, $Z = 8$, and $R = 0.037$ for 8489 reflections having $I \geqslant 3\sigma(I)$. The $[Rh_5(CO)_{14}(CH_2CN)]^-$ anion contains an elongated trigonal-bipyramidal metallic framework bearing eight terminal and six edge-bridging carbonyls; the alkyl-like substituent is bonded to an apical Rh atom.

It has often been claimed that cluster compounds are possible models for heterogeneous catalysis, and they have even been proposed as homogeneous catalysts themselves.[1] Metal–alkyl species are often supposed to be formed at the active metal sites in many heterogeneously catalyzed reactions, but until recently, only a few osmium or rhenium clusters bearing an alkyl or alkyl-like ligand had been reported,[2] although many clusters with μ-carbene or -carbyne groups are known.

In a recent paper[3] we reported the synthesis of two iridium–alkyl clusters: $[PPh_4][Ir_4(CO)_{11}(CH_2COOMe)]$ and $[PPh_4]_2[Ir_4(CO)_{10}(CH_2COOMe)_2]$, starting from $Na[Ir(CO)_4]$ and $BrCH_2COOMe$. Here, we report our results concerning the related reaction of $[Cat][Rh(CO)_4]$ (Cat = Na, PPh_4) with a deficiency of $BrCH_2COOMe$ and $BrCH_2CN$ with respect to the 1:1 molar ratio. The reaction of $[PPN][Rh(CO)_4]$ [$PPN^+ = (PPh_3)_2N^+$] with a stoichiometric quantity of $BrCH_2COOMe$ or $BrCH_2CN$ has been previously reported by some of us as giving selectively the mononuclear compounds $[RhBr(CO)_2(CH_2R)]^-$ (R = COOMe, CN).[4]

Results and Discussion

When a THF solution of $[PPh_4][Rh(CO)_4]$[5] (**1**) is treated with a small amount of $BrCH_2COOMe$ or $BrCH_2CN$, an immediate reaction takes place, with vigorous CO evolution, yielding $[PPh_4][RhBr(CO)_2(CH_2R)]$ (R = COOMe (**2a**), CN(**2b**)).[4] All the organic bromide is consumed in a few minutes. This solution, still containing the excess **1**, upon standing reacts further (ca. 4 h in the case of **2a** and 2 h for **2b**), giving, as the only carbonyl products, two clusters (R = COOMe (**3a**), CN(**3b**)). Their IR absorption pattern is similar to that of the compounds of general formula $[Rh_5(CO)_{14}X]^{2-}$[6] (X = halide or pseudo-halide), thus suggesting structural similarity (vide infra).

$$\underset{\mathbf{1}}{[PPh_4][Rh(CO)_4]} \xrightarrow[-CO]{BrCH_2R} \underset{\mathbf{2a,b}}{[PPh_4][RhBr(CO)_2(CH_2R)]} \xrightarrow{Rh(CO)_4^-} \underset{\mathbf{3a,b}}{[PPh_4]_2[Rh_5(CO)_{14}(CH_2R)]} \quad (1)$$

The IR spectrum of **3a** also displayed an absorption band at 1675 cm^{-1}, assigned to the ν_{CO} stretching of the COOMe group, while **3b** showed an absorption at 2183

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