ELSEVIER

Journal of Organometallic Chemistry 493 (1995) 175–179

Journal of Organometallic Chemistry

Syntheses and structural studies of two adducts of cadmocene, $[CdCp_2.TMEDA]$ and $[CdCp_2.PMDETA]$ ($TMEDA = Me_2NCH_2CH_2NMe_2$, $PMDETA = (Me_2NCH_2CH_2)_2NMe$)

Donald Barr [a], Andrew J. Edwards [b], Paul R. Raithby [b], Moira-Ann Rennie [b],
Kerry L. Verhorevoort [b], Dominic S. Wright [b],*

[a] *Associated Octel Co. Ltd., P.O. Box 17, Oil Sites Road, Ellesmere Port, South Wirral L65 4HF, UK*
[b] *University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, UK*

Received 12 October 1994

Abstract

$Cp_2Cd.TMEDA$ **1** and $Cp_2Cd.PMDETA$ **2** have been synthesized and characterized by spectroscopic studies and by X-ray diffraction studies at low-temperature (153 K). The adducts are present in the crystals as mononuclear complexes. When the denticity of the Lewis base ligands in these adducts is increased (from two in **1** to three in three in **2**) the Cd^{2+} centre requires less electron density from the Cp ligands and the hapticity changes from η^{2-} in **1** to η^{1-} in **2**. Complexes **1** and **2** are the first compounds for which π-bonding of Cp ligands to Cd^{2+} has been observed in the solid state.

Keywords: Cadmium; Metallocene; Crystal structure; Cadmocene; Adducts; X-ray diffraction

---

1. Introduction

We have recently used nucleophilic addition and substitution reactions of heavy p block metal cyclopentadienyl ($C_5H_5^-$) derivatives of Groups 13 (E = Tl) and 14 (E = Sn, Pb) in the syntheses of a variety of organometallic complexes [1–7]. The metal centres in these species can accept weak nucleophiles such as Cp^- to produce a range of complexes containing anionic organometallic fragments [1–4]. However, more potent nucleophiles, such as imino anions and organometallics will displace the Cp ligands of Cp_2E (E = Sn or Pb), to give anionic and mixed-ligand complexes [5–7]. More recently, we have become interested in the syntheses and structures of Group 12 organometallics (Zn, Cd, Hg) [8,9] which are potential precursors of semi-conducting films [10]. Nucleophilic substitution and addition reactions of dicyclopentadienylcadmium $[Cp_2Cd]$ provide potential routes to a range of Cd organometallic and metallo-organic derivatives. Although the synthesis of cadmocene was reported by Lorberth twenty five years ago [11], very little is known about its chemistry. As a prelude to the investigation of the interaction of nucleophiles with $[Cp_2Cd]$ we have investigated its adducts with Lewis base ligands. We report the syntheses and structural properties of two neutral adducts $[CdCp_2.TMEDA]$, **1**, and $[CdCp_2.PMDETA]$, **2** [$TMEDA = Me_2NCH_2CH_2NMe_2$ and $PMDETA = (Me_2NCH_2CH_2)_2NMe$]. The structural characterization of **1** and **2** allows, for the first time, an investigation of the factors affecting the hapticity of the Cp ligands within a series of cadmocene adducts. In contrast to the previously reported neutral adduct $[CdCp_2.2py]$ **3** (py = pyridine) in which there is σ-attachment of the Cp ligands [12], complex **1** has the Cp ligands (η^{2-}) π-bonded to the Cd centre. This is the first compound in which π-bonding of Cp to Cd^{2+} has been observed in the solid state.

2. Results and discussions

$[Cp_2Cd.TMEDA]$, **1**, and $[Cp_2Cd.PMDETA]$, **2**, were prepared in good yields (65% for **1** and 75% for **2**) by the 1:1 reactions of $[Cp_2Cd]$ with TMEDA and

---

* Corresponding author.

SSDI 0022-328X(95)05325-1

Table 1
Selected bond distances (Å) and angles (°) for [Cp_2Cd.TMEDA] **1** and [Cp_2Cd.PMDETA] **2**

	Cp_2Cd.TMEDA	Cp_2Cd.PMDETA
Cd–C(11)	2.426(6)	2.397(6)
Cd–C(12)	2.453(8)	
Cd–C(21)	2.344(5)	2.410(6)
Cd–C(22)	2.743(5)	
Cd–N(1)	2.394(4)	2.430(5)
Cd–N(2)	2.426(6)	2.573(5)
Cd–N(3)		2.492(5)
C(11)–C(12)	1.383(12)	1.440(11)
C(12)–C(13)	1.372(11)	1.379(11)
C(13)–C(14)	1.400(9)	1.426(12)
C(14)–C(15)	1.364(9)	1.362(11)
C(15)–C(11)	1.410(9)	1.455(11)
C(21)–C(22)	1.415(9)	1.418(11)
C(22)–C(23)	1.399(9)	1.379(10)
C(23)–C(24)	1.400(8)	1.438(10)
C(24)–C(25)	1.397(9)	1.352(10)
C(25)–C(21)	1.417(9)	1.430(9)
C(11)–Cd–C(12)	32.9(3)	
C(21)–Cd–C(22)	31.1(2)	
C(11)–Cd–C(21)		111.4(2)
N(1)–Cd–N(2)	77.91(14)	73.21(2)
N(2)–Cd–N(3)		110.3(14)
N(1)–Cd–N(3)		130.7(2)

PMDETA, resspectively, in toluene. Both of these complexes and cadmocene are highly air- and moisture-sensitive, and the use of thoughly dried and degassed solvents, Lewis base donors and dry O_2-free argon is essential in their preparation (particularly in order to avoid the formation of insoluble cadmium hydroxide). Complexes **1** and **2** are fairly stable thermally, and as solids can be stored indefinitely under dry, anaerobic conditions at room temperature.

The complexes were initially characterised by elemental analysis (C, H, N) and by IR and ^1H NMR. spectroscopy (see Tables 1 and 2), which established the identities and stoichiometries of both complexes, later confirmed by X-ray diffraction studies, details of which are in Table 3.

Table 3
Crystal data and details of structural refinements for [Cp_2Cd.TMEDA] **1** and [Cp_2Cd.PMDETA] **2**

	Compound **1**	Compound **2**
Formula	$C_{16}H_{26}CdN_2$	$C_{19}H_{33}CdN_3$
M	358.79	415.88
Crystal system	monoclinic	orthorhobic
Space group	$P2_1/c$	$P2_12_12_1$
a(Å)	12.115(2)	9.693(2)
b(Å)	10.327(2)	9.782(2)
c(Å)	13.327(3)	20.725(4)
β(°)	95.72(3)	90
V(Å^3)	1659.1(6)	1965.1(7)
Z	4	4
D_c(Mg m^{-3})	1.436	1.406
F(000)	736	864
Radiation	Mo Kα	Mo Kα
λ(Å)	0.71073	0.71073
μ(mm^{-1})	1.307	1.115
Total no. of reflections	2271	2998
Total no. of independent reflections	2161	2569
No. of refined parameters	188	213
$R1\,[F > 4\sigma(F)]$ (2512 reflections)	0.0261	0.0212
$wR2$ (all data)	0.1111	0.1174

$wR1 = \Sigma \| F_o - |F_c\| / \Sigma |F_o|$ and $wR2 = \{[\Sigma w(F_o^2 - F_c^2)^2] / \Sigma w F_o^4\}^{0.5}$, $w = 1/[\sigma^2(F_o^2) + (xP)^2 + yP]$, $P = (F_o^2 + 2F_c^2)/3$, $x = 0.0926$, $y = 1.04$.

Tables 4 and 5 give the atomic coordinates and equivalent isotropic thermal parameters for **1** and **2** respectively, and Table 1 shows key bond lengths and angles within both complexes.

Complex **1** has a mononuclear structure in which the the Cd centre has a distorted (formally) six-coordinate geometry (Fig. 1). The distortion is probably primarily a result of the bite angle and bulk of the bidentate Lewis base ligand involved. Unlike the pyridine adduct [12], in which both of the cyclopentadienyl rings are monohapto-bonded to cadmium, **1** exhibits η^2- bonding of the Cp ligands. Although this is the case, there is a significant difference in the bonding to the two rings

Table 2
Cyclopentadienyl C–C bond lengths (Å) in some adducts of [Cp_2Cd] and related compounds

Compounds	C–C distances C(11)–C(12)	C(12)–C(13)	C(13)–C(14)	C(14)–C(15)	C(15)–C(11)
$CpSiH_3$	1.500	1.389	1.43	(1.389)	(1.500)
CpNa.TMEDA	1.387	1.375	1.402	1.366	1.376
Cp_2Cd.2py	1.408(6)	1.371(6)	1.382(7)	1.365(7)	1.407(6)
Cp_2Cd.TMEDA	1.383(12)	1.372(11)	1.400(9)	1.364(9)	1.410(9)
Cp_2Cd.PMDETA	1.440(1)	1.379(11)	1.426(12)	1.362(11)	1.455(11)
	C(21)–C(22)	C(22)–C(23)	C(23)–C(24)	C(24)–C(25)	C(25)–C(21)
$CpSiH_3$	1.500	1.389	1.43	(1.389)	(1.500)
CpNa.TMEDA	1.387	1.375	1.402	1.366	1.376
Cp_2Cd.2py	1.373(8)	1.341(8)	1.356(8)	1.331(8)	1.387(7)
Cp_2Cd.TMEDA	1.415(9)	1.399(9)	1.400(8)	1.397(9)	1.417(9)
Cp_2Cd.PMDETA	1.418(10)	1.379(10)	1.438(10)	1.362(11)	1.455(11)

Table 4
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å} \times 10^3$) for **1**. U_{eq} is defined as one third of the trace of the orthogonalised U_{ij} tensor

Atom	x	y	z	U_{eq}
Cd(1)	2619(1)	1241(1)	2424(1)	24(1)
N(1)	2693(3)	−375(4)	3717(3)	27(1)
N(2)	2108(3)	−659(4)	1490(3)	26(1)
C(1)	3731(5)	−303(6)	4392(4)	52(2)
C(2)	1757(4)	−232(5)	4323(4)	40(1)
C(3)	2641(5)	−1623(5)	3171(4)	42(1)
C(4)	1827(5)	−1610(5)	2259(4)	43(1)
C(5)	3003(5)	−1157(5)	940(5)	43(1)
C(6)	1124(5)	−441(6)	770(4)	51(2)
C(11)	4473(6)	2154(6)	2577(6)	56(2)
C(12)	3988(7)	2559(8)	1647(8)	69(3)
C(13)	4400(6)	1842(6)	902(5)	61(2)
C(14)	5172(5)	971(5)	1373(5)	51(2)
C(15)	5224(6)	1160(5)	2390(5)	53(2)
C(21)	918(5)	2262(6)	2590(5)	42(2)
C(22)	1421(5)	3017(5)	3396(4)	43(1)
C(23)	1678(5)	4221(6)	2999(4)	51(2)
C(24)	1330(5)	4216(5)	1965(5)	50(2)
C(25)	853(5)	3017(6)	1698(5)	47(2)

[Cd–C(21) 2.344(5) Å, Cd–C(22) 2.743(5) Å; c.f. Cd–C(11) 2.426(6) Å, Cd–C(12) 2.453(8) Å].

Complex **2** also has a mononuclear structure in the solid state, in which the Cd atom has a distorted trigonal bipyramidal geometry, with the cyclopentadienyl rings monohapto-bonded to the cadmium centre (Fig. 2).

Table 5
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å} \times 10^3$) for **2**. U_{eq} is defined as one third of the trace of the orthogonalised U_{ij} tensor

Atom	x	y	z	U_{eq}
Cd(1)	1666(1)	9148(1)	8586(1)	15(1)
N(1)	3288(5)	10946(5)	8306(3)	22(1)
N(2)	1392(5)	11044(5)	9436(2)	21(1)
N(3)	−812(5)	9268(6)	8902(2)	23(1)
C(1)	4638(7)	10375(7)	8124(4)	29(2)
C(2)	2719(8)	11730(7)	7761(3)	29(2)
C(3)	3474(8)	11840(6)	8871(3)	25(1)
C(4)	2121(7)	12246(6)	9167(3)	24(1)
C(5)	1971(8)	10637(8)	10056(3)	35(2)
C(6)	−85(8)	11317(7)	9521(3)	30(2)
C(7)	−902(7)	10004(8)	9528(3)	28(2)
C(8)	−1592(7)	10014(10)	8388(4)	42(2)
C(9)	−1393(8)	7878(7)	8976(3)	35(2)
C(11)	2383(8)	7444(7)	9347(3)	34(2)
C(12)	2137(8)	6204(7)	8990(4)	33(2)
C(13)	3366(8)	5809(7)	8712(3)	38(2)
C(14)	4419(9)	6774(8)	8866(4)	38(2)
C(15)	3839(8)	7744(7)	9252(3)	34(2)
C(21)	1063(7)	8142(7)	7562(3)	25(2)
C(22)	2455(8)	7863(7)	7397(3)	26(2)
C(23)	2750(8)	8557(7)	6834(3)	27(2)
C(24)	1517(7)	9262(7)	6638(3)	28(2)
C(25)	507(7)	9011(7)	7072(3)	25(1)

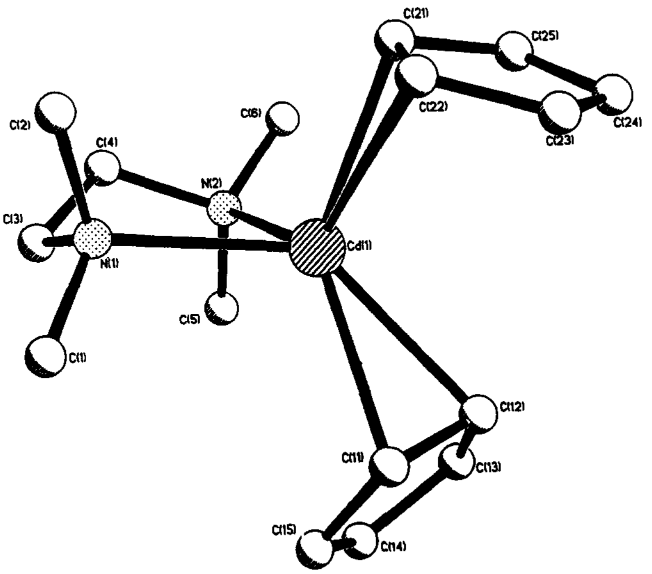

Fig. 1. Crystal Structure of [Cp_2Cd.TMEDA], **1**.

The C–C bond lengths within the cyclopentadienyl rings of [Cp_2Cd.TMEDA], **1**, [Cp_2Cd.PMDETA] **2**, [Cp_2Cd.2py] **3** [12], [CpNa.TMEDA] [13] and [$CpSiH_3$] [14] are compared in Table 2. The compound $CpSiH_3$, represents an example in which the Cp ring is largely covalently bonded while CpNa.TMEDA is an example of a structure in which there is a predominant ionic interaction between the Cp ligand and a metal centre.

In $CpSiH_3$, the C–C bond lengths of the Cp ligand alternate in a manner consistent with a largely covalent interaction between Si and C(1), with double-bond character for the C(2)–C(3) and C(4)–C(5) bonds and conjugation allowing partial double-bond character for C(3)–C(4) (with an associated decrease in bond length)

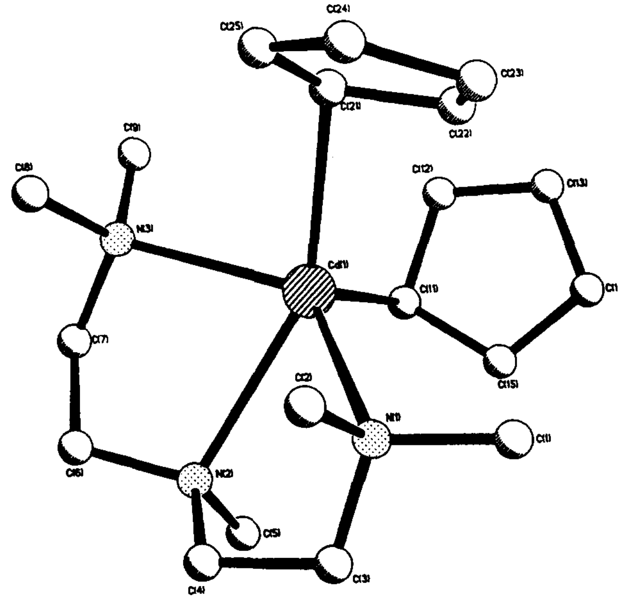

Fig. 2. Crystal Structure of [Cp_2Cd.PMDETA], **2**.

Table 6
^{1}H NMR data for [Cp_2Cd.TMEDA] **1** and [Cp_2Cd.PMDETA] **2**

Compound	Solvent	C_5H_5 (ppm)	Donor (ppm)
Cp_2Cd	d_5-pyridine	6.60 (s, 10H)	
Cp_2Cd.TMEDA	d_5-pyridine	6.58 (s, 10H)	2.18 (s, 12H), 2.37 (s, 4H)
Cp_2Cd.PMDETA	d_5-pyridine	6.54 (s, 10H)	2.16 (s, 3H), 2.21 (s, 12H), 2.38 (t, 6 Hz, 4H), 2.50 (t, 6Hz, 4H)

[14]. In the case of [CpNa.TMEDA] [13], in which all the C–C bond lengths are approximately equal, the cyclopentadienyl ligand can be considered as Cp^-. Comparison of the structures of the cadmocene adducts (**1**–**3**) with the two above extremes reveals that as the number and/or denticity of the donors in these adducts increases the M–Cp interaction moves progressively towards monohapto and tends towards the pattern found in $CpSiH_3$. This trend is no doubt a result of the Cd^{2+} centre progressively requiring less electron density from the Cp ligands as the metal centre is electronically satisfied by the Lewis base donors. However, judging by the similarity of the C–C bond lengths in **1**–**3** with those in [CpNa.TMEDA] [13], the Cp–Cd interactions are still largely ionic in these adducts regardless of the hapticity of the Cp ligands.

In general, the cadmium centre in R_2Cd compounds is usually a very weak acceptor, as shown by the fact that only a few stable coordination complexes of the type $R_2Cd.2L$ are known. A number of Group 12 metal alkyl adducts with nitrogenous bases were reported nearly 30 years ago by Thiele [15–19], but were shown to undergo extensive dissociation in solution. The absence of dissociation for [Cp_2Cd.2py], **3**, in solution has been attributed to the relatively strong electron-withdrawing character of the cyclopentadienyl groups compared to alkyl substituents, which results in an increase in the Lewis acidity of the cadmium centre [12]. This suggestion appears to be confirmed by a comparison of the C–N bonds in the recent X-ray structure [Me_2Cd.TMEDA] (av. 2.570 Å) [20] with those in **1** (av. 2.41 Å). The Cd–N bonds in the cadmocene adduct are substantially shorter and presumably stronger. Presumably this increased stability of the Cd–N bonds is also responsible for the apparent absence of dissociation for complexes **1** and **2** in solution (as indicated by NMR spectroscopy).

3. Conclusions

The results significantly increase knowledge of the structural chemistry of the neutral adducts of cadmium species. They allow a comparison of the effects of different donors upon the $CdCp_2$ fragment in the adducts [$CdCp_2$.TMEDA], **1**, [$CdCp_2$.PMDETA], **2**, and [$CdCp_2$.2py], **3**. As the denticity of the Lewis base ligands in these adducts increases, the M–Cp interaction becomes progressively more monohapto and tends towards the pattern found in $CpSiH_3$. The Cd^{2+} centre requires less electron density from the Cp ligands and the hapticity moves from η^2- to η^1-. Additionally, all the Cp–Cd interactions in these complexes are predominently ionic. Complex **1** is the first compound in which π-bonding of Cp to Cd^{2+} has been observed in the solid state.

This series of cadmocene adducts can be compared with a similar series of dialkylcadmium adducts. Comparison of the Cd–N bond lengths in [Me_2Cd.TMEDA] with those in [Cp_2Cd.TMEDA], **1**, shows that the Cd–N bonds in the cadmocene adduct are substantially stronger. The increased stability of the Cd–N bonds in the cadmocene adducts is evidenced by the fact that they do not undergo any detectable dissociation in solution.

4. Experimental details

All compounds were prepared under dry O_2 free argon using standard inert atmosphere techniques [21]. Syntheses were carried out in Schlenk tubes on a vacuum line and dry samples for analytical, IR and NMR studies were handled in a glove box (Belle Technology) fitted with an internal recirculation system within a Faircrest shell. The $CdCp_2$ was synthesized from $Cd[N(SiMe_3)_2]_2$ and freshly distilled cyclopentadiene as previously described [11]. All chemicals were purchased from Aldrich. Solvents were freshly distilled over Na/benzophenone and degassed prior to use. Organic donors (PMDETA, TMEDA) were dried over a molecular sieve (13X).

Elemental compositions (C, H, N) were determined using a Perkin-Elmer 240 Elemental Analyser, samples being sealed in air-tight aluminium boats prior to analysis. IR spectra (recorded as Nujol mulls) were pre-

Table 7
IR data for **1** and **2**

Compound	Cp–H stretch (cm^{-1})	aromatic $C\overset{\cdots}{-}C$ (cm^{-1})
Cp_2Cd	3170	1608
Cp_2Cd.TMEDA	3056, 3065, 3078	1607
Cp_2Cd.PMDETA	3074, 3062, 3051	1574

pared in the glove-box and were recorded on a Perkin-Elmer FT-IR spectrophotometer. NMR samples were sealed in air-tight NMR tubes (Wilmad, 528pp) in the glove-box and spectra were obtained with a Bruker WH250 spectrometer. ^1H NMR samples were referenced to the internal solvent peaks (D_5-pyridine, C_6D_4HN at δ 7.0, δ 7.35 and δ 8.5).

X-ray diffraction studies of adducts **1** and **2** were performed at 153 K Crystals of approximate dimensions $0.3 \times 0.3 \times 0.3$ mm were mounted under argon directly from solution using an oil-coating method in which the crystal is protected in a drop of perfluorocarbon oil (Riedel-deHaën) which solidifies, and thus holds the crystal static in the beam at low temperatures [22]. Data were collected by the θ/ω method ($7° \leq 2\theta \leq 45°$) on a Stoe-Siemens AED diffractometer equipped with an Oxford Cryostream cooling system. The structure was solved by direct methods (SHELXTL PLUS) and refined by full-matrix least-squares on F^2 (SHELXL-93, Göttingen, 1993). Crystal data and details of intensity measurements are given in Table 5. A complete list of bond distances and angles, and tables of thermal parameters and hydrogen atom coordinates have been deposited at the Cambridge Crystallographic Data Centre.

4.1. [CdCp$_2$.TMEDA], 1.

To a solution of 2.5 mmol (0.606 g) of cadmocene in 10 ml of freshly distilled toluene was added 0.38 ml (2.5 mmol) of TMEDA. The yellow solution was stirred at room temperature for 5 mins and the volume then reduced in vacuo to 5 ml. Colourless, air-sensitive crystals of **1** were obtained in 65% yield (230 mg, first batch) after 24 h at −10°C. The crystals decomposed, without melting, above 130°C. Anal. Found: C, 49.2; H, 6.5; N, 7.0. Calc.: C, 53.5; H, 7.3; N, 7.8%. The difference between experimental and calculated elemental values can be attributed to the air sensitivity of the sample.

4.2. CdCp$_2$.PMDETA, 2.

To a solution of 2.5 mmol (0.606 g) of cadmocene in 10 ml of freshly distilled tetrahydrofuran was added 0.44 ml (2.5 mmol) of PMDETA. The red solution was stirred at room temperature for 5 mins and the volume the reduced in vacuo to 5 ml. Colourless, air-sensitive crystals of **2** were obtained in 75% yield (310 mg, first batch) after 24 h at −10°C. Melting point 90–91°C. Anal. Found: C, 60.7; H, 6.1; N, 6.7. Calc.: C, 61.3; H, 6.1; N, 6.5%.

Acknowledgements

We gratefully acknowledge support by the EPSRC (A.J.E., P.R.R., K.L.V., D.S.W.), the Associated Octel Co. Ltd., (K.L.V., D.S.W.), and the Royal Society (D.S.W.), and the cooperation of the Cambridge Crystallographic Data Centre (M.-A.R.).

References

[1] M.G. Davidson, D. Stalke and D.S. Wright, *Angew. Chem.*, *104* (1992) 1265; *Angew. Chem.*, *Int. Edn. Engl.*, *31* (1992) 1226.

[2] D.R. Armstrong, R. Herbst-Irmer, A. Kuhn, D. Moncrieff, M.A. Paver, C.A. Russell, D. Stalke, A. Steiner and D.S. Wright, *Angew. Chem.*, *105* (1993) 1807; *Angew. Chem.*, *Int. Edn. Engl.*, *32* (1993) 1774.

[3] A.J. Edwards, M.A. Paver, P.R. Raithby, C.A. Russell, D. Stalke and D.S. Wright, *J. Chem. Soc.*, *Dalton Trans.*, (1993) 1465.

[4] D.R. Armstrong, M.G. Davidson, D. Moncrieff, C.A. Russell, D. Stalke, A. Steiner and D.S. Wright, *J. Am. Chem. Soc.*, in preparation.

[5] M.A. Paver, D. Stalke and D.S. Wright, *Angew. Chem.*, *105* (1993) 445; *Angew. Chem.*, *Int. Edn. Engl.*, *32* (1993) 428.

[6] M.A. Paver, C.A. Russell, D. Stalke and D.S. Wright, *J. Chem. Soc.*, *Chem. Commun.*, (1993) 1349.

[7] A.J. Edwards, M.A. Paver, P.R. Raithby, C.A. Russell and D.S. Wright, *J. Chem. Soc.*, *Chem. Commun.*, (1993) 1086.

[8] M.G. Davidson, D. Elilio, S.L. Less, A. Martin, P.R. Raithby, R. Snaith and D.S. Wright, *Organometallics*, (1993) 1.

[9] A.J. Edwards, M.A. Paver, P.R. Raithby, C.A. Russell and D.S. Wright, *Organometallics*, *12* (1993) 4687.

[10] (a) M.L. Steigerwald and C.R. Sprinkle, *J. Am. Chem. Soc.*, *109* (1987) 7200; (b) M.L. Steigerwald, A.P. Alivisatos, J.M. Gibson, T.D. Harris, R. Kortan, A.J. Muller, A.M. Thayer, T.M. Duncan, D.C. Douglass and L.E. Brus, *J. Am. Chem. Soc.*, *110* (1988) 3046; (c) E.K. Bryne, L. Parkanyi and K.H. Theopold, *Science*, *241* (1988) 332; (d) R.L. Wells, C.G. Pitt, A.T. McPhail, A.P. Purdy, S. Shafieezad and R.B. Hallock, *Chem. Mater.* 1 (1989) 4; (e) M.D. Healy, P.E. Laibinis, P.D. Stupik and A.R. Barron, *J. Chem. Soc.*, *Chem. Commun.*, (1989) 359; (f) S.M. Stuczynski, J.G. Brennan and M.L. Steigerwald, *Inorg. Chem. 28* (1989) 4431; See also, *J. Organomet. Chem.*, (1993) 449, and references therein.

[11] J. Lorberth, *J. Organomet. Chem.*, *19* (1969) 189.

[12] J. Boersma, B. Fischer, W.J.J. Smeets, A.L. Spek and G.P.M. v. Meer, *J. Organomet. Chem.*, *322* (1987) C37–C40.

[13] T. Aoyagi, H.M.M. Shearer, K. Wade and G. Whitehead, *J. Organomet. Chem.*, *175* (1979) 21.

[14] D. Damiani, L. Ferretti and E. Gallinella, *Chem. Phys. Lett.*, *37* (1976) 265.

[15] K.H. Thiele, *Z. Anorg. Allg. Chem.*, *319* (1962) 183.

[16] K.H. Thiele, *Z. Anorg. Allg. Chem.*, *322* (1963) 71.

[17] K.H. Thiele, *Z. Anorg. Allg. Chem.*, *325* (1963) 156.

[18] K.H. Thiele, *Z. Anorg. Allg. Chem.*, *330* (1964) 8.

[19] K.H. Thiele, *Z. Anorg. Allg. Chem.*, *156* (1968) 156.

[20] P. O'Brien, M.B. Hursthouse, A.C. Jones, M. Motevalli and J.R. Walsh, *J. Organomet. Chem.*, *449* (1993) 1.

[21] D.F. Shriver and M.A. Drezdon, *The Manipulation of Air-Sensitive Compounds*, 2nd edn., Wiley, NY, 1986.

[22] T. Kottke and D. Stalke, *J. Appl. Crystallogr.*, *26* (1993) 615.