

Synthesis and structural characterization of magnesium and cobalt derivatives of the bulky aryl ligand $-\text{C}_6\text{H}_3-2,6-\text{Mes}_2$

Jeffrey J. Ellison, Philip P. Power *

Department of Chemistry, University of California, Davis, CA 95616, USA

Received 19 March 1996; revised 17 May 1996

Abstract

The synthesis and structural characterization of the new metal-terphenyl derivatives $[\text{BrMC}_6\text{H}_3-2,6-\text{Mes}_2(\text{THF})_2]$ ($\text{M} = \text{Mg}$ (1), Co (2); $\text{Mes} = -\text{C}_6\text{H}_2-2,4,6-\text{Me}_3$) are described. The magnesium derivative 1 was synthesized by reaction of the previously known iodide $\text{IC}_6\text{H}_3-2,6-\text{Mes}_2$ with activated magnesium. Subsequent treatment of 1 with CoCl_2 affords 2 in moderate yield. Compounds 1 and 2 have very similar dimeric structures, in which two bromides bridge two metals. Each metal is also coordinated to a $-\text{C}_6\text{H}_3-2,6-\text{Mes}_2$ group and a THF molecule. The metals are thus four-coordinated. The cobalt species 2 is a very unusual example of a stable Co(II) σ -bonded hydrocarbyl. The Co–Co separation of ca. 3.5 Å precludes the existence of significant metal–metal bonding. Crystal data at 130 K with $\text{Mo K}\alpha$ ($\lambda = 0.71073$ Å) radiation: 1, $a = 9.432(2)$, $b = 21.973(5)$, $c = 12.558(2)$ Å, $\beta = 94.87(2)^\circ$, $Z = 2$, monoclinic, space group $P2_1/c$, $R = 0.058$ for 3006 ($I > 2\sigma(I)$) data, 2, $a = 9.394(2)$, $b = 22.033(7)$, $c = 12.390(3)$ Å, $\beta = 94.99(2)^\circ$, $Z = 2$, monoclinic, space group $P2_1/c$, $R = 0.077$ for 2675 ($I > 2\sigma(I)$) data.

Keywords: Magnesium; Cobalt; Aryl; Bromide; Crystal structure

1. Introduction

Over the past two decades there has been an ever expanding interest in the synthesis of very sterically demanding ligands and their applications in the kinetic stabilization of unusual valencies or bonding, as well as low coordinate environments, in a large range of transition metal and main group compounds. Hydrocarbyl ligands [1] (i.e. ligands that bind through carbon and involve C–H bonded substituents) have played a major role in this area. The most common hydrocarbyl groups are either alkyls or aryls, and of these two the chemistry of the alkyls is the most highly developed from the point of view of steric effects. However, sterically encumbered aryl ligands had not been the subject of systematic exploration in the same way as bulky alkyl ligands such as $-\text{CH}(\text{SiMe}_3)_2$ [2] or $-\text{C}(\text{SiMe}_3)_3$ [3] until after ca. 1980. The discovery of compounds such as $\text{Mes}_2\text{Si}=\text{SiMes}_2$ [4] and $\text{Mes}^*\text{P}=\text{PMes}^*$ [5] ($\text{Mes} = -\text{C}_6\text{H}_2-2,4,6-\text{Me}_3$; $\text{Mes}^* = -\text{C}_6\text{H}_2-2,4,6-\text{tBu}_3$) in the early 1980s has led to a more widespread use of bulky aryl ligands to achieve a high degree of crowding

in derivatives of a variety of elements throughout the periodic table. The most notable of these ligands is the Mes^* group [5], featuring *ortho*- ^tBu substituents which has been shown to stabilize two-coordination in magnesium [6], manganese [6] and iron [6,7] (more recent examples of bulky aryls include $-\text{C}_6\text{H}_3-2,6(\text{SiMe}_3)_2$ and $-\text{C}_6\text{H}_2-2,4,6(\text{CH}(\text{SiMe}_3)_2)_3$, see Ref. [8]). The pursuit of increasingly crowded environments has led us to examine the use of *m*-terphenyl ligands $-\text{C}_6\text{H}_3-2,6-\text{Ar}_2$ for this purpose ($\text{Ar} = \text{Mes}$ [9], Dipp [10] or Trip [10]; $\text{Dipp} = -\text{C}_6\text{H}_3-2,6-\text{tPr}_2$, $\text{Trip} = \text{C}_6\text{H}_2-2,4,6-\text{tPr}_3$). For example, it has been demonstrated that terphenyl substituents at sulfur or selenium in thiolate and selenolate ligands, i.e. in $-\text{E}(\text{C}_6\text{H}_3-2,6-\text{Mes}_2)$ ($\text{E} = \text{S}$ or Se), can effect two-coordination in the monomeric species $\text{M}\{\text{E}(\text{C}_6\text{H}_3-2,6-\text{Mes}_2)\}_2$ ($\text{E} = \text{S}$ [11,12] or Se [13]; $\text{M} = \text{Mg}$ [12], Fe [11], Mn [13], Zn [11]). Structural studies have also shown that the unsolvated aryl lithium derivative has the dimeric formula $(\text{LiC}_6\text{H}_3-2,6-\text{Mes}_2)_2$ [9], which is at present the lowest degree of aggregation for an uncomplexed aryl lithium compound. In addition, $\text{Et}_2\text{OLiC}_6\text{H}_3-2,6-\text{Trip}_2$ [10] has a monomeric structure with a two-coordinate lithium ion. Furthermore, application of this ligand to gallium chemistry has resulted in

* Corresponding author.

an unusual, almost T-shaped geometry in the bisaryl derivative $\text{ClGa}(\text{C}_6\text{H}_3\text{-2,6-Mes}_2)_2$ [14] and the stabilization of a novel, formally aromatic 2π -electron, Ga_3 ring in the compound $\text{Na}_2(\text{GaC}_6\text{H}_3\text{-2,6-Mes}_2)_3$ [15]. The synthesis and structure of two new derivatives involving the elements magnesium and cobalt are now reported.

2. Experimental section

2.1. General procedures

All experiments were performed under a nitrogen atmosphere either by using modified Schlenk techniques or in a Vacuum Atmospheres HE 43-2 drybox. Solvents were freshly distilled from a sodium–potassium alloy and degassed twice prior to use. ^{13}C , ^1H , and ^7Li NMR spectra were recorded in C_6D_6 or C_7D_8 solutions by using a General Electric QE-300 NMR spectrometer. IR data were recorded as Nujol mulls on a Perkin–Elmer 1430 spectrometer. Magnetic measurements were performed on a Johnson–Matthey magnetic balance. $n\text{-BuLi}$ (1.6M solution in hexanes) was purchased commercially and used as received. $\text{IC}_6\text{H}_3\text{-2,6-Mes}_2$ [16] and $(\text{LiC}_6\text{H}_3\text{-2,6-Mes}_2)_2$ [9] were prepared by literature procedures.

2.2. $[\text{BrMgC}_6\text{H}_3\text{-2,6-Mes}_2(\text{THF})]_2$

$\text{IC}_6\text{H}_3\text{-2,6-Mes}_2$ (1.76 g, 4 mmol) was added via a solid addition funnel to a THF (75 ml) suspension of

activated [17] magnesium (9 mmol). The solution was stirred overnight and then filtered through a layer of Celite. The THF was then removed under reduced pressure and the remaining white residue was extracted with toluene (50 ml). The volume was reduced to incipient crystallization and cooled overnight in a -20°C freezer to afford colorless crystals of the product in ca. 70% yield; m.p. $182\text{--}186^\circ\text{C}$. Anal. Found: C, 68.15; H, 6.69. $\text{C}_{28}\text{H}_{33}\text{BrMg}_2\text{O}$ Calc.: C, 68.67; H, 6.79%. ^1H NMR ($\text{PhMe-}d_8$) δ 1.89 (br, s, 4H, THF), 2.05 (s, 6H, p-Me), 3.84 (br, s, 4H, THF), 6.94 (t, 1H, p-H), 7.10 (d, 2H m-H(Ph)), 7.46 (s, 4H m-H(Mes)). $^{13}\text{C}\{^1\text{H}\}$ NMR ($\text{PhMe-}d_8$) 20.4–21.2 (various Me and THF carbons), 127.3–128.5 (various m and p carbons), 130.0–141.4 (various quaternary carbons). IR (Nujol, ν cm^{-1}): 1945 w, 1870 w, 1800 w, 1765 w, 1730 w, 1705 w, 1610 s, 1570 s, 1300 w, 1210 m, 1230 m, 1175 m, 1085 m, 1070 m, 1015 s, 920 m, 900 w, 870 s, 850 s, 800 s, 775 m, 735 s, 710 s, 695 w, 540 s, 500 w, 440 w, 415 w, 385 w, 320 s.

2.3. $[\text{BrCoC}_6\text{H}_3\text{-2,6-Mes}_2(\text{THF})]_2$

$\text{IC}_6\text{H}_3\text{-2,6-Mes}_2$ (1.76 g, 4 mmol) was added via a solid addition funnel to a THF (75 ml) suspension of activated magnesium (9 mmol). The solution was stirred overnight and then filtered through a bed of Celite. CoCl_2 (0.50 g, 4 mmol) was added via a solid addition funnel and the reaction mixture was left to stir overnight. The THF was removed from the resultant blue solution under reduced pressure and the remaining blue precipi-

Table 1
Selected data collection parameters for $[\text{BrMC}_6\text{H}_3\text{-2,6-Mes}_2(\text{THF})]_2$ (M = Mg (1) or Co (2))

Compound	$[\text{BrMgC}_6\text{H}_3\text{-2,6-Mes}_2(\text{THF})]_2$	$[\text{BrCoC}_6\text{H}_3\text{-2,6-Mes}_2(\text{THF})]_2$
Formula	$\text{C}_{36}\text{H}_{66}\text{Br}_2\text{Mg}_2\text{O}_2$	$\text{C}_{36}\text{H}_{66}\text{Br}_2\text{Co}_2\text{O}_2$
FW	979.6	1048.8
Crystal color and habit	colorless prisms	navy blue prisms
Crystal size (mm)	$0.36 \times 0.48 \times 0.72$	$0.30 \times 0.40 \times 0.65$
a (\AA)	9.423(2)	9.394(2)
b (\AA)	21.973(5)	22.033(7)
c (\AA)	12.558(2)	12.393(3)
β ($^\circ$)	94.87(2)	94.99(2)
V (\AA^3)	2590.7(9)	2555.5(12)
Z	2	2
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
$d(\text{calc})$ (g cm^{-3})	1.256	1.363
Linear abs. coeff.	1.627	2.252
Trans. coeff.	0.34–0.61	0.27–0.58
2θ range ($^\circ$)	0–52.0	0–50.0
No. unique data	5097	4514
Obs. refl.	3006 ($I > 2.0\sigma(I)$)	2675 ($I > 3.0\sigma(I)$)
No. variables	280	280
R^2 , R_w^2	0.058, 0.059	0.077, 0.126

$R = \sum |F_o| - |F_c| / \sum |F_o|$, $R_w = \sum |F_o| - |F_c| w^{1/2} / \sum |F_o| w^{1/2}$ and $w = 1/\sigma^2(F_o) + GF_o^2$. Data were collected at 130 K using Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$).

tate was extracted with toluene (25 ml) and filtered. The volume was reduced to incipient crystallization and cooled overnight in a -20°C freezer, producing dark blue crystals of the product in ca. 60% yield; m.p. 140°C (decomp.). Anal. Found: C, 64.82; H, 6.31. $\text{C}_{28}\text{H}_{33}\text{BrCoO}$ Calc.: C, 64.13; H, 6.34%. ^1H NMR (PhMe-d_6) (300 K) δ -4.01 (s, br, 4H, THF), 1.86 (s, 6H, *p*-Me), 2.12 (s, 12H, *o*-Me), 3.09 (s, br, 4H, THF), 6.65 – 7.26 (various aryl protons). IR (Nujol, ν (cm^{-1})): 1905 w, 1845 w, 1785 w, 1725 w, 1610 m, 1565 w, 1545 w, 1305 w, 1260 w, 1220 m, 1165 m, 1120 w, 1095 m, 1070 s, 1020 s, 950 w, 910 w, 870 s, 850 s, 795 s, 770 w, 740 m, 725 s, 690 m, 610 w, 565 w, 545 w, 500 w, 460 w, 410 w, 345 m, 330 m, 280 m. UV-vis (nm) (ϵ): 710 (180), 559 (180), 392 (155); $\mu_{\text{eff}} = 4.7$ at 298 K.

2.4. X-ray data collection, the solution and refinement of the structures

The crystals were coated with a layer of hydrocarbon oil upon removal from the Schlenk tube. Suitable crystals were selected, attached to a glass fiber, and immediately placed in the low-temperature N_2 -stream [18]. X-ray data were collected with a Siemens R3 m/V diffractometer equipped with a graphite monochromator and a locally modified LT apparatus. Calculations were carried out on a MicroVax 3200 computer using the SHELXTL-PLUS [19] program system. Neutral atom scattering factors and the correction for anomalous dispersion were those supplied with SHELXTL-PLUS. The structures were solved by direct methods. The data were subsequently refined by full-matrix least-squares procedures. Hydrogen atoms were included by the use of a riding model with C–H distances of 0.96 Å and fixed isotropic thermal parameters with $U_{\text{H}}(\text{iso}) = 0.06$ Å². An abbreviated list of data collection parameters and some important structural details are provided in Tables 1 and 2 respectively.

Table 2
Some important bond distances (Å) and angles ($^{\circ}$) for $[\text{BrMC}_6\text{H}_3\text{-2,6-Mes}_2(\text{THF})_2]$ (M = Mg (1) or Co (2))

	Mg (1)	Co (2)
M–C	2.132(6)	2.053(8)
M–O	2.012(4)	2.023(8)
M–Br	2.559(2)	2.480(2)
	2.579(2)	2.495(2)
M...M	3.621(2)	3.520(2)
Br–M–Br'	90.4(1)	89.9(1)
M–Br–M'	89.6(1)	90.1(1)
Br–M–C	126.3(2)	126.1(2)
Br'–M–C	125.0(2)	125.7(2)

2.5. Structural descriptions

$[\text{BrMgC}_6\text{H}_3\text{-2,6-Mes}_2(\text{THF})_2]$ and $[\text{BrCoC}_6\text{H}_3\text{-2,6-Mes}_2(\text{THF})_2]$ are isostructural with each other. Each asymmetric unit consists of half a dimeric molecule, each half being related to the other by an inversion center. The two bromide atoms bridge the metals forming an almost perfectly square M_2Br_2 core. The metals are each bound to a terminal THF molecule and a terminal $-\text{C}_6\text{H}_3\text{-2,6-Mes}_2$ group, and thus are four-coordinated. The two crystallographically independent M–Br bridging distances are almost equal and the internal M_2Br_2 ring angles at M and Br are very close to 90° . The mutually *trans*-orientation of both the THF and aryl ligands as well as the planar nature of the central M_2Br_2 arrays are, of course, required by crystallographic symmetry. The metal–metal distances are $3.621(2)$ Å (Mg) and $3.520(2)$ Å (Co). Further details are given in Table 2.

3. Discussion

The reaction between $\text{IC}_6\text{H}_3\text{-2,6-Mes}_2$ [16] and activated magnesium [17] affords the Grignard compound **1** in good yield. The appearance of the bromide instead of iodide in the formula of **1** (and **2**) arises from the use of 'activated' magnesium which is a mixture of magnesium metal and MgBr_2 . Attempts were also made to disproportionate **1** with 1,4-dioxane into the presently uncharacterized bisaryl $\text{Mg}(\text{C}_6\text{H}_3\text{-2,6-Mes}_2)_2$ and the $\text{MgBr}_2(1,4\text{-dioxane})_2$ co-product in a manner similar to the preparation of MgMes_2^+ [6]. Although precipitation of the adduct was evident upon the addition of 1,4-dioxane, the magnesium diaryl has not been obtained in a pure state and crystals suitable for X-ray studies have not yet been obtained. Parallel experiments involving the cobalt derivative **2** gave similar results.

The structural characteristics of Grignard reagents and other classes of organomagnesium compounds have recently been reviewed [20]. Typically, the Grignard reagents feature a coordination number of four at magnesium and include donor molecules (usually THF or Et_2O) bound to magnesium. Four-coordination at Mg in **1** is a little surprising in view of the large size of the $-\text{C}_6\text{H}_3\text{-2,6-Mes}_2$ substituent. Nonetheless, it is evident from Fig. 1 that the coordination at the magnesiums is very distorted from idealized tetrahedral. It is notable that the sum of the interligand angles at magnesium, involving the two bromides and the aryl group, is $341.7(2)^{\circ}$. In effect the angles at the metal indicate that the geometry is well on its way towards a trigonal bipyramidal arrangement in which one of the axial sites is unoccupied. A similar argument may be made for the metal coordination in the cobalt compound **2**. The structure of **1** bears some similarity to those of the bridged

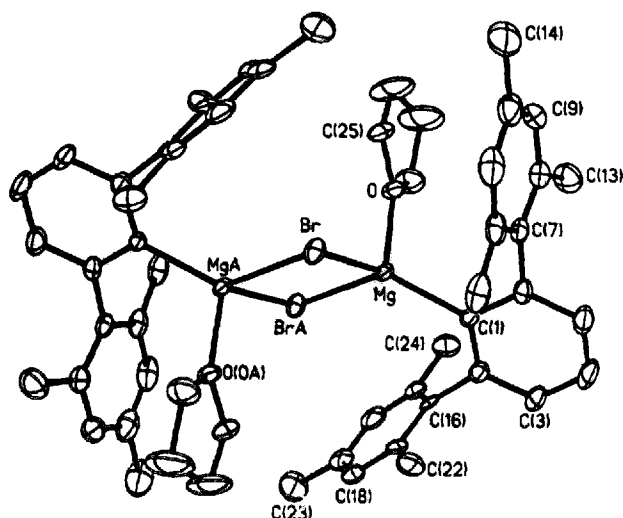


Fig. 1. Thermal ellipsoid plot (30%) of **1**. H atoms are omitted for clarity.

dimers $[\text{BrMgEt}(\text{O}^i\text{Pr})_2]_2$ [21] and $[\text{BrMgEt}(\text{NEt}_3)]_2$ [22]. The observation of dimeric structures in the latter species has led to speculation that structures of this type result only when the compounds are crystallized from a weakly coordinating solvent, i.e. O^iPr_2 or NEt_3 . It has been suggested that, for steric reasons, these solvents were too weakly coordinating to effect dissociation of the organomagnesium complexes into the monomers that are normally observed when Grignards are crystallized from diethyl ether or tetrahydrofuran. A more recent structural report of a Grignard–THF adduct with bridging halides in the compound $[\mu\text{-BrMg}(2\text{-MeOCH}_2\text{C}_6\text{H}_4)(\text{THF})_2]_2$ [23] appears to contradict this interpretation. This structure is, however, atypical of most organomagnesium compounds in that the aryl ligand is bidentate and chelating and results in a coordination number of five at the metal center. In **1** the magnesium center is four-coordinate and the donor solvent is THF. In this case it may be that the steric bulk of the aryl ligand, which prevents the coordination of additional THF ligands to the crowded metal ion, produces the bridged halide dimer structure if not the hoped for three-coordinate monomer. The observed Mg–O distance is 2.012(4) Å, which is shorter than that in the five-coordinate species $[\text{BrMg}(2\text{-MeOCH}_2\text{C}_6\text{H}_4)(\text{THF})_2]_2$, 2.070(5) Å (av.), and is very similar to that seen in the four-coordinate dimer $[\text{BrMgEt}(\text{O}^i\text{Pr})_2]_2$, 2.019(6) Å. The bridging Mg–Br distances in the latter species, 2.582(3) and 2.576(3) Å, are also comparable with those in **1** (cf. Table 2).

The cobalt species **2** is isostructural with **1** and represents a rare example of structurally characterized Co(II) aryl derivative (Fig. 2). In a wider context it may be noted that transition metal species with metal–aryl σ -bonds constitute an important class of compounds in their own right [24]. Homo- and heteroleptic aryl deriva-

tives that are stable in the absence of stabilizing donor ligands such as phosphines or carbonyls are of particular interest. Until recently, the number of well-characterized compounds was relatively few and even at present there are significantly fewer well-characterized homoleptic aryls than alkyls. In the case of Co(II) compounds such species appear to be confined to the anionic derivatives $\text{Li}_2(\text{THF})_4\text{CoPh}_4$ (unstable in solution) [25], $[\text{N}(\text{n-Bu})_4]_2[\text{Co}(\text{C}_6\text{X}_5)_4]$ (X = F or Cl) [26], $[\text{LiCoMes}_3]$ [27,28], a few complexes of multidentate ligands [29] such as 2,6-(MeO) $_2\text{C}_6\text{H}_3^-$, and the neutral dimer $\text{MesCo}(\mu\text{-Mes})_2\text{CoMes}$ [28]. The latter compound with three-coordinate cobalts has also been structurally characterized. One objective of the work described here was to explore the use of the bulky aryl $-\text{C}_6\text{H}_3\text{-2,6-Mes}_2$ in the stabilization of unstable species such as Co(II) derivatives or of two-coordinate, open-shell, transition metal complexes [30] of formula $\text{M}(\text{C}_6\text{H}_3\text{-2,6-Mes}_2)_2$. Since it is apparent that three, or in some cases four, mesityl groups can saturate the coordination environment of a first row transition metal [24,31], it was thought that two $-\text{C}_6\text{H}_3\text{-2,6-Mes}_2$ groups incorporating four mesityl substituents would have sufficient bulk to stabilize a two-coordinate, first row, transition metal environment.

Attempts were made to synthesize such a two-coordinate cobalt diaryl by the reaction of the Grignard reagent with CoBr_2 in a 2:1 ratio. However, only the monosubstituted organocobalt(II) halide dimer **2** has been isolated in a pure state thus far. It has already been noted that there is a close correspondence [32] between the structural parameters of **2** and those of its magnesium analogue. This is consistent with the close similarity of the Shannon–Prewitt radii [33] of the four-coordinate Mg^{2+} (0.71 Å) and the high-spin four-coordinate Co^{2+} (0.72 Å) ions. The Co–C distance may also be com-

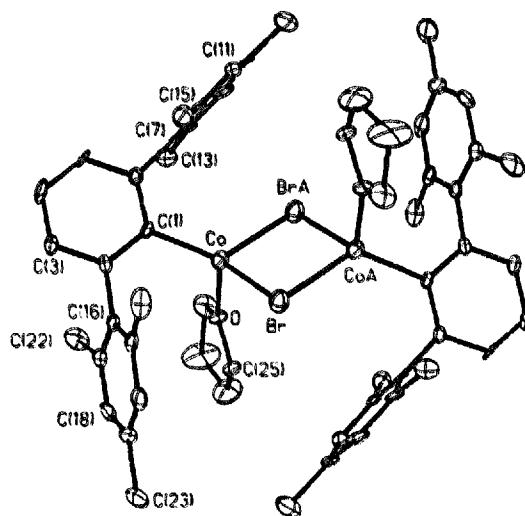


Fig. 2. Thermal ellipsoid plot (30%) of **2**. H atoms are omitted for clarity.

pared with the average terminal Co–C bond length (1.984(5) Å) in MesCo(μ-Mes)₂CoMes [28]. The longer Co–C distance in the bromide derivative may be attributed to the higher coordination number of the metals. The most striking difference between the two cobalt compounds, however, is the metal–metal separation which, in the case of the mesityl derivative, averages 2.516(4) Å. This value is more than 1 Å shorter than the 3.520(2) Å distance observed in [BrCoC₆H₃-2,6-Mes₂(THF)]₂. The structure of MesCo(μ-Mes)₂CoMes, together with the spectroscopic and magnetic studies, is indicative of considerable metal–metal bonding [28]. The magnetic moment measured for [BrCoC₆H₃-2,6-Mes₂(THF)], 4.7 μ_{eff} (at 298 K), is significantly greater than that of MesCo(μ-Mes)₂CoMes at the same temperature, but is nonetheless indicative of some antiferromagnetic coupling since it is less than what would be expected from two high-spin Co²⁺ centers. Clearly, the metal–metal interaction in **2** is greatly reduced in comparison with MesCo(μ-Mes)₂CoMes, most probably as a result of the increased coordination number of the cobalts and the greater distances associated with the bridging region imposed by the longer Co–Br bonds. The stability of the bromo aryl derivative is also remarkable (m.p. 140°C) in view of the fact that the MesCo(μ-Mes)₂CoMes was reported to decompose slowly at room temperature [28]. In view of this encouraging result for the –C₆H₃-2,6 derivative of cobalt it is possible that the –C₆H₃-2,6-Mes₂ ligand will prove effective in the stabilization of other open-shell, transition metal aryls. These investigations are now in hand.

Acknowledgements

We are grateful to the National Science Foundation and the Donors of the Petroleum Research Fund administered by the American Chemical Society for financial support. We also thank Dr. R.J. Wehmschulte for his assistance with the structural data.

References

- [1] P.J. Davidson, M.F. Lappert and R. Pearce, *Chem. Rev.*, **76** (1976) 219.
- [2] M.F. Lappert, in A.R. Bassindale and P.G. Gaspar (eds.), *Frontiers of Organosilicon Chemistry*, Royal Society of Chemistry, Cambridge, 1991, p. 231.
- [3] C. Eaborn, J.D. Smith and K. Izod, *J. Organomet. Chem.*, **500** (1995) 89.
- [4] R. West, M.J. Fink and J. Michl, *Science*, **214** (1981) 1343.
- [5] M. Yoshifuji, I. Shima, N. Inamoto, K. Hirotsu and T. Higuchi, *J. Am. Chem. Soc.*, **103** (1981) 4587.
- [6] R.J. Wehmschulte and P.P. Power, *Organometallics*, **14** (1995) 3264.
- [7] H. Müller, W. Siedel and H. Görls, *Angew. Chem., Int. Ed. Engl.*, **36** (1995) 325.
- [8] E. Block, V. Eswarakrishnan, M. Gernon, G. Ofori-Okai, C. Taka, K. Tang and J. Zubietta, *J. Am. Chem. Soc.*, **111** (1989) 658; N. Tokitoh, K. Manmaru and R. Okazaki, *Organometallics*, **13** (1994) 167.
- [9] K. Ruhlandt-Senge, J.J. Ellison, R.J. Wehmschulte, F. Pauer and P.P. Power, *J. Am. Chem. Soc.*, **115** (1993) 11353.
- [10] B. Schiemenz and P.P. Power, *Organometallics*, **13** (1996) 958.
- [11] J.J. Ellison, K. Ruhlandt-Senge and P.P. Power, *Angew. Chem., Int. Ed. Engl.*, **33** (1994) 1000.
- [12] J.J. Ellison and P.P. Power, *Inorg. Chem.*, **33** (1994) 4231.
- [13] J.J. Ellison, K. Ruhlandt-Senge, H. Hope and P.P. Power, *Inorg. Chem.*, **34** (1995) 49.
- [14] X.-W. Li, W.T. Pennington and G. Robinson, *Organometallics*, **14** (1995) 2109.
- [15] X.-W. Li, W.T. Pennington and G.H. Robinson, *J. Am. Chem. Soc.*, **117** (1995) 7578.
- [16] U. Lüning, C. Wangnick, K. Peters and H.G. von Schnering, *Chem. Ber.*, **124** (1991) 397.
- [17] R.D. Rieke, P.T. Li, T.P. Burns and S.T. Ulm, *J. Org. Chem.*, **46** (1981) 4323.
- [18] H. Hope, in A.L. Wayda and M.Y. Darensbourg (eds.), *Experimental Organometallic Chemistry: A Practicum in Synthesis and Characterization*, ACS Symp. Ser. 357, American Chemical Society, Washington, DC, 1987, Chap. 10, p. 257.
- [19] G.M. Sheldrick, SHELXL-PLUS, *A Program Package for Refinement of Crystal Structures*, University of Göttingen, 1989.
- [20] P.R. Markies, O.S. Akkerman, F. Bickelhaupt, W.J. Smeets and A.L. Spek, *Adv. Organomet. Chem.*, **32** (1991) 147.
- [21] A.L. Spek, P. Voorbergen, G. Schat, C. Bloomberg and F. Bickelhaupt, *J. Organomet. Chem.*, **77** (1974) 147.
- [22] J. Toney and G.D. Stucky, *J. Chem. Soc., Chem. Commun.*, (1967) 1168.
- [23] P.R. Markies, G. Schat, S. Griffioen, A. Villena, O.S. Akkerman and F. Bickelhaupt, *Organometallics*, **10** (1991) 153.
- [24] S.U. Koschmeider and G. Wilkinson, *Polyhedron*, **10** (1991) 135.
- [25] R. Taube and N. Stransky, *Z. Anorg. Allg. Chem.*, **490** (1982) 91.
- [26] R. Uson and J. Fornies, *Adv. Organomet. Chem.*, **28** (1988) 219.
- [27] B. Sarry and M. Schön, *Zh. Chem.*, **8** (1968) 151.
- [28] K. Theopold, J. Silvestre, E.K. Byrne and D.S. Richeson, *Organometallics*, **8** (1989) 2001.
- [29] H. Dreves, *Zh. Chem.*, **15** (1975) 451; **18** (1987) 31.
- [30] P.P. Power, *Chemtracts Inorg. Chem.*, **6** (1994) 181.
- [31] T. Glowiak, R. Grobelny and B. Jesowska-Trzebiatowska, *J. Organomet. Chem.*, **155** (1978) 39.
- [32] Oddly, there is an inverse relationship between the metal-anionic ligand and metal-neutral ligand bond distances in **1** and **2**.
- [33] R.D. Shannon and C.T. Prewitt, *Acta Crystallogr.* **B25** (1969) 925.