Arene Coordination to Yttrium(III) via Carbon−Carbon Bond Formation

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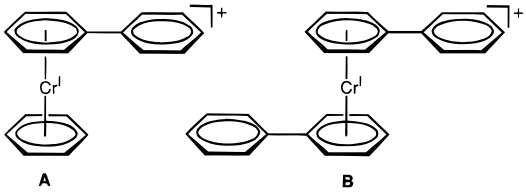
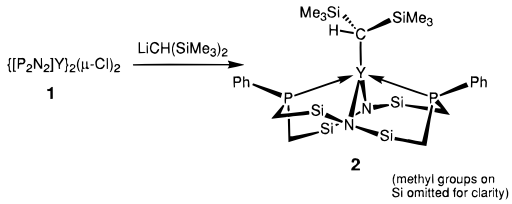
Received June 16, 1997

The synthesis and structural elucidation of the prototypical arene complex, bis(benzene)chromium, $Cr(\eta^6\text{-}C_6H_6)_2$, represents a significant chapter in the development of organometallic chemistry.[1] However, even predating this work are the investigations described by Hein in the early 1920s and 1930s which involved reaction of $CrCl_3$ with excess phenyl-Grignard (PhMgBr). The nature of these products was not unraveled until the 1950s, and it is now generally accepted that the Hein reactions produce bis(arene) Cr(I) derivatives by the transformation of an η^1-aryl group to a coordinated η^6-arene unit;[2] two of the major components of the Hein reactions were found to be the Cr(I) biphenyl cations $[Cr(\eta^6\text{-}C_6H_6)(\eta^6\text{-}C_6H_5{-}C_6H_5)]^+$ (**A**) and $[Cr(\eta^6\text{-}C_6H_5{-}C_6H_5)_2]^+$ (**B**), formed via an aryl coupling/reduction sequence. In the course of examining some yttrium(III) alkyl chemistry, we discovered a series of highly colored arene complexes of Y(III) that apparently involve C−H activation followed by carbon−carbon bond coupling. The fact that



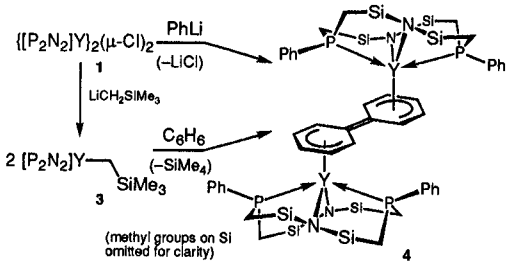
an η^1-aryl group attached to yttrium is undergoing a transformation to generate an η^6-arene is reminiscent of the early Hein work; however, the arene-type complexes of yttrium(III) reported here are significantly different than the well-studied arene complexes of the middle and late transition metals.

As part of our interest in the coordination chemistry of the phosphorus-containing macrocycle, *syn*-$[P_2N_2]$ ($[P_2N_2]$ = $[PhP(CH_2SiMe_2NSiMe_2CH_2)_2PPh]$),[3] we examined the preparation of yttrium(III) complexes incorporating this new ancillary ligand system. The chloride-bridged dimer $\{[P_2N_2]Y\}_2(\mu\text{-}Cl)_2$ (**1**), prepared in 95% yield by reaction of *syn*-$Li_2(THF)[P_2N_2]$ with $YCl_3(THF)_3$ in tetrahydrofuran (THF), can be converted to mononuclear alkyl species by straightforward metathesis using alkyllithium reagents. Addition of the very bulky $LiCH(SiMe_3)_2$ to **1** leads to the formation of $Y\{CH(SiMe_3)_2\}[P_2N_2]$ (**2**) in 92% yield. Both the solution spectroscopic data[4] and the X-ray



crystal structure indicated that **2** is monomeric, with the yttrium atom adopting a distorted square-based pyramidal geometry, the

Scheme 1



$[P_2N_2]$ ligand in the basal plane, and the $CH(SiMe_3)_2$ unit apical.[4−7] The utilization of the less sterically hindered alkyl moiety CH_2SiMe_3 resulted in the yttrium neosilyl complex $Y(CH_2SiMe_3)[P_2N_2]$ (**3**), which could only be isolated as an oil from hexanes. As with **2**, the multiplicity of the methylene protons of the CH_2SiMe_3 group in the ^1H NMR spectrum suggests that **3** is monomeric in solution.[8] Addition of THF to a solution of **3** in toluene results in the formation of the THF adduct $Y(CH_2SiMe_3)(THF)[P_2N_2]$ (**3**·THF), isolated from hexanes as a colorless solid.

Although the bulkier yttrium alkyl derivative **2** was found to be quite thermally robust in aromatic solvents, the THF-free neosilyl complex **3** was less stable and prone to the formation of deep blue solutions. When the reaction between **1** and $LiCH_2SiMe_3$ was monitored in a mixture of C_6D_6/C_6H_6 at ambient temperature by $^{31}P\{^1H\}$ NMR spectroscopy, the immediately formed neosilyl complex **3** (δ_P −32.1, d, $^1J_{YP}$ = 81.0 Hz) slowly transformed into a new product **4** (δ_P −25.2, d, $^1J_{YP}$ = 84.9 Hz); solutions of **4** are intensely blue (λ_{max} 616 nm, ϵ_o 13 000 L mol^{-1} cm^{-1}). From the ^1H NMR spectrum of **4**, it was evident that $SiMe_4$ had been eliminated, presumably via an intermolecular σ-bond metathesis reaction[9] with the benzene solvent, with new resonances observed for one aryl group per $[P_2N_2]Y$ fragment, albeit dramatically shifted upfield to 5.10 (2H), 4.46 (2H), and 4.18 ppm (1H), a shift indicative of π-type interaction with the yttrium.[10] On the basis of the NMR spectroscopic parameters and the microanalytical data, an empirical formula for **4** as $Y(C_6H_5)[P_2N_2]$ was supportable. This formulation suggested that **4** should be accessible via the direct reaction of the chloride-bridged dimer **1** with phenyllithium; indeed, this is the case (Scheme 1).

An X-ray diffraction study was undertaken of the deep blue crystals isolated from hexanes. The molecular structure of **4** is shown in Figure 1 along with selected bond lengths and bond angles.[11] What becomes immediately obvious is that **4** is a dinuclear complex having a biphenyl unit bridging two yttrium $[P_2N_2]$ fragments with each $Y[P_2N_2]$ bound in an η^6-fashion to the opposite faces of the biphenyl moiety. The bonding in this complex can be viewed simplistically as the interaction of two

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(1) Huheey, J. E. *Inorganic Chemistry*, 3rd ed.; Harper & Row: New York, 1983.
(2) Zeiss, H. *Organometallic Chemistry*; ACS Monograph Series; American Chemical Society: Washington, DC, 1960; Vol. 147, p 380.
(3) Fryzuk, M. D.; Love, J. B.; Rettig, S. J. *Chem. Comm.* **1996**, 2783.
(4) Haan, K. H. d.; Boer, J. L. d.; Teuben, J. H.; Spek, A. L.; Kojic-Prodic, B.; Hays, G. R.; Huis, R. *Organometallics* **1986**, *5*, 1726.
(5) Giardello, M. A.; Conticello, V. P.; Brard, L.; Sabat, M.; Rheingold, A. L.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1994**, *116*, 10212.
(6) Duchateau, R.; Wee, C. T. v.; Meetsma, A.; Duijen, P. T. v.; Teuben, J. H. *Organometallics* **1996**, *15*, 2279.
(7) Schaverien, C. J.; Orpen, A. G. *Inorg. Chem.* **1991**, *30*, 4968.
(8) Lee, L.; Berg, D. J.; Einstein, F. W.; Batchelor, R. J. *Organometallics* **1997**, *16*, 1819.
(9) Thompson, M. E.; Baxter, S. M.; Bulls, A. R.; Burger, B. J.; Nolan, M. C.; Santarsiero, B. D.; Schaefer, W. P.; Bercaw, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 203.
(10) Elschenbroich, C.; Salzer, A. *Organometallics, a concise introduction*; VCH Publishers, Inc.: New York, 1992.

(11) Crystal data for **4** $[C_{60}H_{94}N_4P_4Si_8Y_2$ (fw = 1397.82)]: blue prism, monoclinic $P2_1/c$ (No. 14), a = 12.154(1) Å, b = 16.398(2) Å, c = 18.478(1) Å, β = 103.436(7)°, V = 3581.7(6) Å^3, D_{calcd} = 1.296 g/cm^3 (Z = 2), R = 0.039, GOF = 1.87. All other details of the crystal structure are reported in the Supporting Information. Crystal data for **6** $[C_{69}H_{106}N_4P_4Si_8Y_2$ (fw = 1518.01)]: brown prism, monoclinic $P2_1/c$ (No. 14), a = 13.0769(6) Å, b = 26.9793(13) Å, c = 23.6505(2) Å, β = 104.0335(2)°, V = 8095.0(4) Å^3, D_{calcd} = 1.245 g/cm^3 (Z = 4), R = 0.046, GOF = 2.00. All other details of the crystal structure are reported in the Supporting Information.

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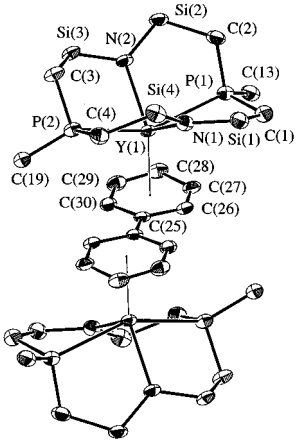

Figure 1. The solid state structure of $\{[P_2N_2]Y\}_2\{\eta^6:\eta^{6'}\text{-}(C_6H_5)_2\}$ **4**. Selected bond lengths (Å) and angles (deg): Y(1)−N(1) 2.313(3), Y(1)−N(2) 2.328(3), Y(1)−P(1) 2.812(1), Y(1)−P(2) 2.931(1), Y(1)−C(25) 2.699(4), Y(1)−C(26) 2.708(4), Y(1)−C(27) 2.733(4), Y(1)−C(28) 2.675(4), Y(1)−C(29) 2.738(4), Y(1)−C(30) 2.722(4), C(25)−C(26) 1.453(6), C(25)−C(25)* 1.393(8), C(25)−C(30) 1.456(5), C(26)−C(27) 1.378(6), C(27)−C(28) 1.415(6), C(28)−C(29) 1.404(6), C(29)−C(30) 1.359(6); N(1)−Y(1)−N(2) 99.2(1), P(1)−Y(1)−P(2) 149.29(4).

yttrium(III) $[P_2N_2]$ fragments with a biphenyl dianion $[Ph-Ph]^{2-}$. The biphenyl dianion in **4** is essentially planar. The bond distance between the two aryl groups (C25−C25*) is 1.393(8) Å, indicative of a C−C double bond; the other bond lengths in the biphenyl unit clearly show short C−C bonds except for those directly attached to the newly formed bond. There is no evidence for ring slippage since all of the Y−C bond distances are similar and range from 2.675(4) to 2.738(4) Å. Also, there is a slight boat conformation in each aryl ring of **4**, although markedly less pronounced than the 25° deviation from planarity of the $C_6H_6^{2-}$ ligand for the complex $[K(18\text{-crown-}6)][La\{\eta^5\text{-}1,3\text{-}C_5H_3(SiMe_3)_2\}_2)(C_6H_6)]$.[12] The biphenyl dianion has been previously structurally characterized in the complex $[(C_5Me_5)Fe]_2(\mu\text{-}\eta^5:\eta^5\text{-biphenyl})$.[13] Unlike **4**, an η^5-coordination mode of the phenyl rings is adopted with a significant 25° angle between the ring planes.

Other aryllithium reagents can be used; for example, the reaction of *m*-tolyllithium with **1** also generates deep blue solutions from which blue crystals of **5** could be isolated in modest yield. The ^1H NMR spectral data suggest an unsymmetrical geometry, since all eight protons of the bi-*m*-tolyl fragment are inequivalent; the UV−vis spectrum is virtually identical to **4**. However, the reaction of *p*-tolyllithium with **1** generated a dark orange-brown solution, from which dark brown crystals of **6** could be isolated in good yield. The ^1H NMR spectrum indicated the presence of a π-bound *p*-Me-C_6H_4 unit due to the upfield shift of these aromatic resonances: a tightly coupled AB doublet of doublets was observed centred at 4.15 ppm. The solid state molecular structure (Figure 2) showed that a bridging bi-*p*-tolyl unit was present; however, in this complex both yttrium centers were found to be sandwiching one tolyl group.[11] The bond lengths in the sandwiched tolyl group are indicative of a bis(allyl) distortion while the uncoordinated tolyl moiety is essentially unaffected by the presence of the two proximate Y(III) centers. The aforementioned ^1H NMR spectral data are inconsistent with the solid state structure, since only one type of *p*-tolyl group was observed; a fluxional process was indicated since as the temperature was lowered, broadening of all the signals was observed, and new broad peaks grew in around 6−7 ppm at −95 °C suggestive of an uncoordinated arene. The peaks due to the sandwiched arene are

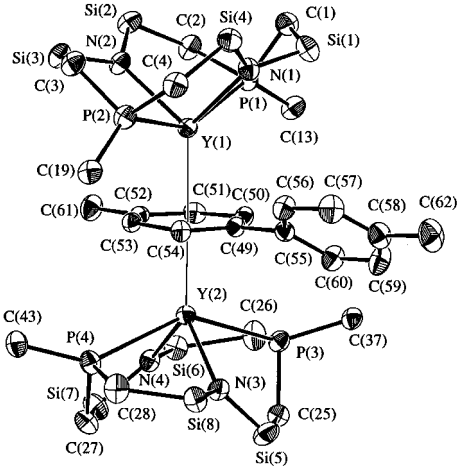

Figure 2. The solid state structure of $\{[P_2N_2]Y\}_2\{\eta^6:\eta^6\text{-}C_6H_4Me\text{-}4(C_6H_4Me\text{-}4')\}$ **6**. Selected bond lengths (Å) and angles (deg): Y(1)−N(1) 2.330(3), Y(1)−N(2) 2.353(3), Y(1)−P(1) 2.8750(11), Y(1)−P(2) 2.8513(11), Y(1)−C(49) 2.692(4), Y(1)−C(50) 2.661(4), Y(1)−C(51) 2.699(4), Y(1)−C(52) 2.693(4), Y(1)−C(53) 2.629(4), Y(1)−C(54) 2.680(4), Y(2)−C_{av} 2.699, C(49)−C(50) 1.399(5), C(49)−C(54) 1.431(5), C(49)−C(55) 1.481(5), C(50)−C(51) 1.508(5), C(51)−C(52) 1.414(5), C(52)−C(53) 1.394(5), C(53)−C(54) 1.508(5); C−C_{av} (uncoordinated ring) 1.384(5); N(1)−Y(1)−N(2) 100.84(11), P(1)−Y(1)−P(2) 151.08(4); inter-ring twist angle 38.2°.

presumed to be masked beneath the broadened ligand resonances in the 0−2 ppm region. Thus, at low temperatures in solution, a similar structure to that observed in the solid state is observed but at higher temperatures, the two $Y[P_2N_2]$ fragments migrate from one *p*-tolyl group to the other on the NMR time scale. Such a fluxional process is remarkable given the nature of the different distortions in the biaryl unit observed in the solid state structures of both **4** and **6**, particularly since both structures are presumably involved in this dynamic behavior.

In all three cases described above, a rearrangement from an unobserved yttrium derivative having a σ-bound aryl group to a dinuclear complex with both yttrium centers π-bound has occurred. We speculate that the key intermediate is a dimer with bridging aryl groups that couple to generate the observed π-bound species. In contrast to the Hein chemistry discussed above, the biaryl couplings reported here do not involve any formal redox chemistry, since the yttrium center starts as Y(III) and finishes in the same oxidation level. This contrasts other lanthanoid arene systems that have been prepared via reductive sequences[14−16] or by metal vapor techniques.[17] Phenyl groups bridging lanthanoid metals are not well established;[18] a few examples of mononuclear σ-aryl complexes are known for yttrium but few have been structurally characterized.[19−21] Reactivity studies of these dinuclear bis(arene) complexes are underway.

Acknowledgment. NSERC of Canada is gratefully acknowledged for financial support of this work.

Supporting Information Available: Detailed experimental procedures, spectroscopic data, and X-ray structural details for **4** and **6** (49 pages). See any current masthead page for ordering and Internet access instructions.

JA9719743

(12) Cassani, M. C.; Gun'ko, Y. K.; Hitchcock, P. B.; Lappert, M. F. *Chem. Commun.* **1996**, 1987.
(13) Lacoste, M.; Rabaa, H.; Astruc, D.; Ardoin, N.; Varret, F.; Saillard, J.-Y. *J. Am. Chem. Soc.* **1990**, *112*, 9458.
(14) Cotton, F. A.; Schwotzer, W. *J. Am. Chem. Soc.* **1986**, *108*, 4657.
(15) Cotton, F. A.; Schwotzer, W. *Organometallics* **1987**, *6*, 1275.
(16) Deacon, J. B.; Shen, Q. *J. Organomet. Chem.* **1996**, *511*, 1.
(17) Cloke, F. G. N. *Chem. Soc. Rev.* **1993**, *1993*, 17.
(18) Schumann, H.; Meese-Markscheffel, J. A.; Esser, L. *Chem. Rev.* **1995**, *95*, 865.
(19) Booij, M.; Kiers, N. H.; Meetsma, A.; Teuben, J. H.; Smeets, W. J. J.; Spek, A. L. *Organometallics* **1989**, *8*, 2454.
(20) Booij, M.; Deelman, B.-J.; Duchateau, R.; Postma, D. S.; Meetsma, A.; Teuben, J. H. *Organometallics* **1993**, *12*, 3531.
(21) Deelman, B.-J.; Stevels, W. M.; Teuben, J. H.; Lakin, M. T.; Spek, A. L. *Organometallics* **1994**, *13*, 3881.