Replacement of a Cyclometalated Terdentate Diamino Ligand by a Phosphorus Analogue. Isolation and Crystallographic Characterization of an Intermediate in Aryl C−H Bond Activation in Models of Dendrimer-Bound Organometallic Catalysts

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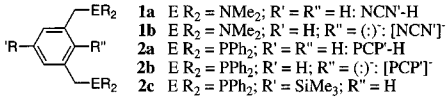
The chemistry of the potentially monoanionic, terdentate diaminoaryl ligand $[NCN']^-$ (**1**) and its phosphorus analogue bisphosphinoaryl $[PCP']^-$ (**2**, Figure 1) have been extensively studied in this laboratory and others[1−3] due to their strong propensity to form stable transition metal (TM) and main-group organometallic complexes, often in unusual geometries and/or oxidation states.[4] A number of these TM compounds are effective catalysts for the synthesis of commodity and fine chemicals, and they have also been used as molecular probes in a number of fundamental chemical processes, notably C−H bond activation.[2−6] We have been interested in using functionalized aryl ligands as templates for the incorporation of catalytically active TM fragments onto polymeric or well-defined carbosilane dendritic supports ("dendrimer catalysts").[7] We report herein some aspects of the chemistry of d^6 Ru(II) PCP′ complexes which are employed as models for TM compounds which are tethered to carbosilane dendrimers.[7c] This work has in turn led to the isolation and characterization (NMR, IR, X-ray Crystallography) of a rare intermediate in aryl C−H bond activation of a PCP′−H ligand. It is also shown that aryl−Si bond cleavage reactions can predominate the chemistry of carbosilane dendrimers incorporating ligand fragments such as $[PCP']^-$ (**2**).



1a E R_2 = NMe_2; R′ = R″ = H: NCN′-H
1b E R_2 = NMe_2; R′ = H; R″ = (:)⁻: $[NCN']^-$
2a E R_2 = PPh_2; R′ = R″ = H: PCP′-H
2b E R_2 = PPh_2; R′ = H; R″ = (:)⁻: $[PCP']^-$
2c E R_2 = PPh_2; R′ = $SiMe_3$; R″ = H

Figure 1.

Treatment of 3,5-$(Ph_2PCH_2)_2C_6H_3Br$ with 2 equiv of ^{t}BuLi at −78 °C produces the lithium compound [3,5-$(Ph_2PCH_2)_2C_6H_3$-Li]$_n$ (**3**). Quenching of **3** with TMS-Cl (TMS = trimethylsilyl) yields the TMS substituted ligand **2c** in 93% isolated yield.[8] This synthesis can be envisioned as a model for the grafting of a PCP′−H ligand to a carbosilane dendrimer which is terminated by reactive -SiR_2Cl groups.[7c,9] Our desire was then to chelate the dendrimer bound PCP′ ligand to a Ru metal center. Ruthenium(II) complexes of this class are known hydrogenation and hydrogen transfer catalysts and can participate in alkyne and aryl coupling reactions.[3] To our surprise, however, treatment of **2c** with the Ru(II) precursor $RuCl_2(PPh_3)_3$[10] led to the isolation in 98% yield of the known *para*-H complex **4a** (Scheme 1; *i.e.*, incorporating the PCP′ fragment **2b**).[3a,b] The high yield of **4a** indicates that aryl−Si bond cleavage (*i.e.*, protondesilylation) is readily facilitated by the reaction conditions.[11] The desilylation of ligand **2c** could not be prevented with the addition of NEt_3. Thus, the direct attachment of a Ru moiety on to a PCP′ terminated carbosilane dendrimer cannot be accomplished in this manner because the subsequent rupturing of the aryl−Si bond will release the resulting complex from the dendrimer framework.

Fortunately, it was discovered that the reaction of the analogous complex RuCl[2,6-$(Me_2NCH_2)_2C_6H_3$](PPh_3) (**5**)[3a,c] reacts with ligand precursor **2c** to give the desired complex **6** in 70% overall yield (Scheme 1).[12] This reaction, which is unprecedented in the organometallic chemistry of tridentate monoanionic ligands, represents a useful synthetic protocol for

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(1) (a) Mayer, H. A.; Kaska, W. C. *Chem. Rev.* **1994**, *94*, 1239−1272. (b) Bianchini, C.; Meli, A.; Peruzzini, M.; Vizza, F.; Zanobini, F. *Coord. Chem. Rev.* **1992**, *120*, 193−208. (c) Cotton, F. A.; Hong, B. *Prog. Inorg. Chem.* **1992**, *40*, 179−290.

(2) (a) van der Kuil, L. A.; Luitges, H.; Grove, D. M.; Zwikker, J. W.; van der Linden, J. G. M.; Roelofsen, A. M.; Jenneskens, L. W.; Drenth, W.; van Koten, G. *Organometallics* **1994**, *3*, 468−477. (b) Steenwinkel, P.; James, S. L.; Grove, D. M.; Veldman, N.; Spek, A. L.; van Koten, G. *Chem. Eur. J.* **1996**, *2*, 1440−1445. (c) Davies, P. J.; Veldman, N.; Grove, D. M.; Spek, A. L.; Lutz, B. T. G.; van Koten, G. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1959−1961.

(3) (a) Karlen, T.; Dani, P.; Grove, D. M.; Steenwinkel, P.; van Koten, G. *Organometallics* **1996**, *15*, 5687−5694. (b) Jia, G.; Lee, H. M.; Xia, H. P.; Williams, I. D. *Organometallics* **1996**, *15*, 5453−5455. (c) Sutter, J.-P.; James, S. L.; Steenwinkel, P.; Karlen, T.; Grove, D. M.; Veldman, N.; Smeets, W. J. J.; Spek, A. L.; van Koten, G. *Organometallics* **1996**, *15*, 941−948. (d) Liou, S.-Y.; Gozin, M.; Milstein, D. *J. Chem. Soc., Chem. Commun.* **1995**, 1965−1966, *J. Am. Chem. Soc.* **1995**, *117*, 9774−9775. (e) Gozin, M.; Weismann, A.; Ben-David, Y.; Milstein, D. *Nature* **1993**, *364*, 699−701. (f) Gozin, M.; Aizenberg, M.; Liou, S.-Y.; Weismann, A.; Ben-David, Y.; Milstein, D. *Nature* **1994**, *370*, 42−44. (g) Kaska, W. C.; Nemeh, S.; Shirazi, A.; Potuznik, S. *Organometallics* **1988**, *7*, 13−15. (h) Creaser, C. S.; Kaska, W. C. *Inorg. Chim. Acta* **1978**, *30*, L325−L326. (i) Gorla, F.; Togni, A.; Venanzi, L. M.; Albinati, A.; Lianza, F. *Organometallics* **1994**, *13*, 1607−1616. (j) Rimml, H.; Venanzi, L. M. *Phosphorus Sulfur* **1987**, *30*, 297−300, and references therein. (k) Vigalok, A.; Ben-David, Y.; Milstein, D. *Organometallics* **1996**, *15*, 1839−1844. (l) Fryzuk, M. D.; Montgomery, C. D.; Rettig, S. J. *Organometallics* **1991**, *10*, 467−473. (m) Moulton, C. J.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1976**, 1020−1024. (n) Perera, S. D.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1995**, 3861−3866. (o) Cross, R. J.; Kennedy, A. R.; Manojlovic-Muir, L.; Muir, K. W. *J. Organomet. Chem.* **1995**, *493*, 243−249. (p) Nemeh, S.; Jensen, C.; Binamira-Soriaga, E.; Kaska, W. C. *Organometallics* **1983**, *2*, 1442−1447. (q) Gupta, M.; Hagen, C.; Kaska, W. C.; Cramer, R. E.; Jensen, C. M. *J. Am. Chem. Soc.* **1997**, *119*, 840−841. (r) Gupta, M.; Hagen, C.; Kaska, W. C.; Flesher, R.; Jensen, C. M. *Chem. Commun.* **1996**, 2083−2084.

(4) (a) van Koten, G. *Pure Appl. Chem.* **1989**, *61*, 1681−1694. (b) Rietveld, M. H. P.; Grove, D. M.; van Koten, G. *New J. Chem.* **1997**, *21*, 751−771.

(5) (a) Grove, D. M.; Verschuuren, A. H. M.; van Koten, G. *J. Mol. Catal.* **1988**, *45*, 169−174. (b) Grove, D. M.; Verschuuren, A. H. M.; van Koten, G.; van Beek, J. A. M. *J. Organomet. Chem.* **1989**, *372*, C1−C6.

(6) (a) Canty, A. J.; van Koten, G. *Acc. Chem. Res.* **1995**, *28*, 406−413. (b) Ryabov, A. D. *Chem. Rev.* **1990**, *90*, 403−424. (c) Green, M. L. H.; O'Hare, D. *Pure Appl. Chem.* **1985**, *57*, 1897−1910.

(7) Polymeric: (a) van der Kuil, L. A.; Grove, D. M.; Zwikker, J. W.; Jenneskens, L. W.; Drenth, W.; van Koten, G. *Chem. Mater.* **1994**, *6*, 1675−1683. (b) Pathmamanoharan, C.; Wijkens, P.; Grove, D. M.; Philipse, A. P. *Langmuir* **1996**, *12*, 4372−4377. Dendrimeric: (c) Knapen, J. W. J.; van der Made, A. W.; de Wilde, J. C.; van Leeuwen, P. W. N. M.; Wijkens, P.; Grove, D. M.; van Koten, G. *Nature* **1994**, *372*, 659−663. Also see: (d) Bhyrappa, P.; Young, J. K.; Moore, J. S.; Suslick, K. S. *J. Mol. Catal. Part A: Chemical* **1996**, *113*, 109−116.

(8) Synthesis of **2c**: Prepared from a reaction of 3,5-$(Ph_2PCH_2)_2C_6H_3$-Br (1.11 g, 2.0 mmol) in Et_2O (30 mL) with ^{t}BuLi (2.1 equiv, 0.6 M pentane solution) at −78 °C, stirred (30 min) and then quenched with TMS-Cl (2.0 mL, 16 mmol). Yield: 1.02 g (93%), colorless oil. For full details see the Supporting Information.

(9) (a) Alonso, B.; Cuadrado, I.; Morán, M.; Losada, J. *J. Chem. Soc., Chem. Commun.* **1994**, 2575−2576. (b) Alonso, B.; Morán, M.; Casado, C. M.; Lobete, F.; Losada, J.; Cuadrado, I. *Chem. Mater.* **1995**, *7*, 1440−1442. (c) Lobete, F.; Cuadrado, I.; Casado, C. M.; Alonso, B.; Morán, M.; Lasada, J. *J. Organomet. Chem.* **1996**, *509*, 109−113.

(10) (a) Hallman, P. S.; Stephenson, T. A.; Wilkinson, G. *Inorg. Syn.* **1970**, *13*, 237−244. (b) Hoffman, P. R.; Caulton, K. G. *J. Am. Chem. Soc.* **1975**, *97*, 4221−4228. (c) La Placa, S. J.; Ibers, J. A. *Inorg. Chem.* **1965**, *4*, 778−783.

(11) (a) von Fritz, G.; Kummer, D. *Z. Anorg. Allg. Chem.* **1961**, *308*, 105−121. (b) Eaborn, C. *Organometallic Compounds of the Group IV Elements*; Vol. 1, MacDiarmid, A. G., Ed.; Marcel Dekker, Inc.: New York, 1968; Chapter 2, pp 105−536.

(12) Synthesis of **6**: A solution of **2c** (0.43 g, 0.78 mmol) in THF (10 mL) was added to a boiling THF (20 mL) solution of **5** (0.46 g, 0.79 mmol), and then refluxed for 8 h. The final product was contaminated with a small amount (<5%) of **1a**. Yield: 0.51 g (70%). For full details see the Supporting Information.

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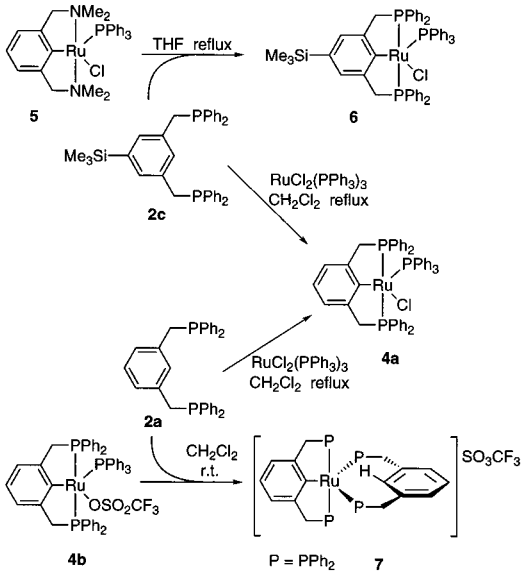
Scheme 1



the incorporation of catalytically active Ru(II) metal centers into carbosilane dendrimers.

The cyclometalation reaction **2c** to **6** must involve an aryl C−H oxidative-addition/reductive-elimination (*i.e.*, aryl C−H bond activation) process. Attempts to monitor the conversion of **5** to **6** *via* NMR spectroscopy revealed the intermediacy of a PCP′−H-bridged Ru dimer.[13] In an attempt to gain further insight into this type of reaction, the examination of the addition of a second equiv of **2a** with the related triflate complex **4b** was undertaken. We chose to use the diphosphine **2a** because its inherit NMR active P atoms would allow for facile spectroscopic investigation. We also felt the use of the known triflate analogue of **4a** (complex **4b**) was prudent as the presence of the triflate anion (kinetically, a good leaving group; although strongly bound to complex **4b**, *cf.* complex **4a**[3a,b]) may enhance the exchange of ligands from the metal coordination sphere. Treatment of **4b** with **2a** in CH_2Cl_2 solution led to the isolation of a yellow diamagnetic complex **7** (Scheme 1).[14] The ^{1}H NMR spectrum of **7** revealed a number of aryl resonances between δ 5.9 and 7.8 ppm in addition to a broad multiplet pattern at δ 3.4 ppm that is assigned to the benzylic C*H*$_2$ protons of the PCP′ fragments. The ^{31}P{^{1}H} NMR spectrum of **7** shows the presence of *four* magnetically distinct P atoms at low temperature.[14] As a conclusive structural assignment of **7** could not be made from the available spectroscopic data, crystals of this compound that were suitable for X-ray structure determination were grown from a solution in CH_2Cl_2/ether/toluene.[15] The ORTEP diagram of **7** is shown in Figure 2 along with selected bond lengths and angles. The location of the hydrogen on C11 of the "incoming" trans-spanning PCP′−H ligand was clearly refined on the final difference map (see Supporting Information)[15] and reveals that this H is pushed out of the plane of the arene ring forming an apparent interaction with the Ru center

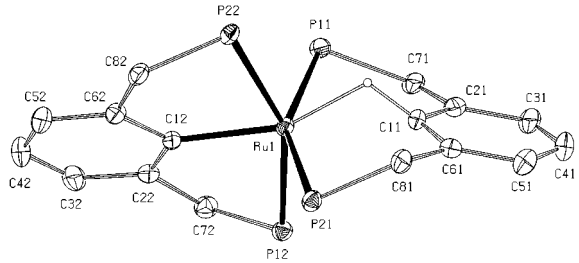


Figure 2. Perspective view (ORTEP, 50% probability) of cation **7**, showing aryl C−H···Ru interaction. Other protons and phenyl groups have been omitted for clarity. Bond distances (Å) and angles (deg): Ru1−P11 2.3732(9), Ru1−P21 2.4432(9), Ru1−P12 2.3716(9), Ru1−P22 2.3575(9), Ru1−C12 2.115(3), Ru1−H 1.76(4), Ru1···C11 2.395(4), C11−H 1.15(4), P11−Ru1−P21 152.74(3), P12−Ru1−P22 153.64(3), P11−Ru1−P12 91.62(3), P11−Ru1−P22 95.89(3), C11−Ru1−C12 171.47(11), Ru1−H−C11 109(3).

of a cationic [PCP′Ru]$^+$ fragment (*i.e.*, either an agostic type C−H···M interaction or a 3c−2e bond are limiting interaction models).[3n,16] The local symmetry around the metal center is best described as a highly distorted octahedral environment. The inequivalence of all four P donor atoms is clearly visible in the structure, and the ^{31}P{^{1}H} NMR data strongly suggest that this geometry is retained in solution. This complex also confirms our recent proposal that chelation of the neutral PCP′−H ligand occurs *via* initial trans coordination of both P atoms and that this precedes electrophilic attack of the metal center on the C−H bond.[3a] Our attempts to observe the appropriate ^{1}H and ^{13}C nuclei of the C−H···Ru interaction have thus far been thwarted by the large number of aromatic resonances and low abundance of the signals of interest. An IR study of **7** did reveal, however, a medium intensity band at 2864 cm^{-1}, which is tentatively assigned to the agostic C−H stretching vibration.[16] Deuteration and ^{1}H, ^{31}P heteronuclear decoupling NMR experiments are currently underway to unequivocally assign the agostic C−H fragment.

In conclusion, this report has shown that the incorporation of reactive Ru(II) PCP′ complexes into carbosilane dendrimers can be accomplished by a facile ligand displacement of the NCN′−H ligand (**1a**) from compound **5**. Attempts to directly add the Ru metal center *via* the traditional precursor $RuCl_2(PPh_3)_3$ leads to aryl−Si bond cleavage and hence would result in degradation of the dendrimer molecule. The direct observation of an intermediate in the C−H bond activation of a neutral PCP′−H ligand has been shown for the first time in these systems and has confirmed that most likely P donor chelation precedes C−H bond activation with a d^6 Ru(II) metal center. We are currently pursuing an extended investigation of this novel C−H bond activation chemistry in addition to the attachment of complexes similar to **6** to dendrimeric macromolecules.

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Supporting Information Available: Tables of crystal data, thermal parameters, bond distances, bond angles, and atomic coordinates for **7** and the ^{31}P{^{1}H} NMR spectra of **7** (210 and 298 K) and the detailed syntheses and NMR data for **2c** and **6** (24 pages). See any current masthead page for ordering and Internet access instructions.

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(13) Full details of this bridged mechanism will be reported separately. It should be noted that the initial displacement of PPh_3 by an incoming PCP′ ligand at room temperature is very rapid for complexes such as **5** and **6**.

(14) Synthesis of **7**: Ligand **2a** (0.47 g, 1.0 mmol) was added to complex **4b** (1.0 g, 1.0 mmol) in CH_2Cl_2 (15 mL). The mixture was stirred at room temperature (0.5 h), and then Et_2O was added to precipitate **7** as an orange solid, which was subsequently washed with Et_2O and dried *in vacuo*. Yield: 0.97 g (81%). ^{1}H NMR (200 MHz, CD_2Cl_2, 298 K): δ 3.10−3.70 (br, 4H, C*H*$_2$), 6.30−7.81 (m, 47 H, Ar*H*). ^{31}P{^{1}H} NMR: The complicated second order spectrum is contained in the Supporting Information. The presence of large *trans* pseudo-coupling constants and smaller *cis* coupling constants strongly suggest that the solid-state structure of **7** is retained in solution. Examination of complex **7** *via* 2D ^{31}P-^{31}P NMR (large couplings are fully resolved) spectroscopy also supports this conclusion. Full details of the NMR characterization of **7** will be reported in a forthcoming full paper. Anal. Calcd (Found) for $C_{65}H_{55}O_3F_3P_4SRu\cdot0.75CH_2Cl_2$: C 62.61 (62.93), H 4.48 (4.56).

(15) Crystal data for **7**: $[C_{64}H_{55}P_4Ru][CF_3O_3S]\cdot CH_2Cl_2\cdot C_4H_{10}O$, M_r = 1357.23, triclinic, space group *P*1, a = 12.7745(11), b = 15.8943(11), c = 17.0745(11) Å, α = 110.669(5), β = 96.973(6), γ = 101.871(6)°, V = 3102.2(4) Å^3, D_x = 1.453 g cm^{-3}, Z = 2, T = 150 K, MoKα, R_1 = 0.0461 for 10 014 reflections with $I > 2\sigma(I)$. The hydrido H was located from a difference map and its position refined.

(16) (a) Brookhart, M.; Green, M. L. H.; Wong, L.-L. *Prog. Inorg. Chem.* **1988**, *36*, 1−124. (b) Crabtree, R.; Hamilton, D. G. *Adv. Organomet. Chem.* **1988**, *28*, 299−338.