Pincer Ligands

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A Cobalt(I) Pincer Complex with an η^2-C$_{aryl}$–H Agostic Bond: Facile C–H Bond Cleavage through Deprotonation, Radical Abstraction, and Oxidative Addition

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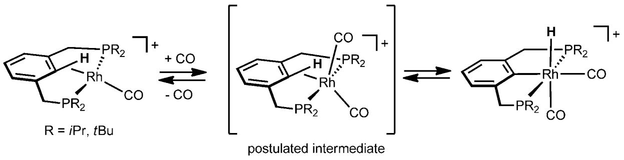
***Abstract:** The synthesis and reactivity of a Co^I pincer complex $[Co(\kappa^3P,CH,P\text{-}P(CH)P^{NMe}\text{-}iPr)(CO)_2]^+$ featuring an η^2-C$_{aryl}$–H agostic bond is described. This complex was obtained by protonation of the Co^I complex $[Co(PCP^{NMe}\text{-}iPr)(CO)_2]$. The Co^{III} hydride complex $[Co(PCP^{NMe}\text{-}iPr)(CNtBu)_2(H)]^+$ was obtained upon protonation of $[Co(PCP^{NMe}\text{-}iPr)(CNtBu)_2]$. Three ways to cleave the agostic C–H bond are presented. First, owing to the acidity of the agostic proton, treatment with pyridine results in facile deprotonation (C–H bond cleavage) and reformation of $[Co(PCP^{NMe}\text{-}iPr)(CO)_2]$. Second, C–H bond cleavage is achieved upon exposure of $[Co(\kappa^3P,CH,P\text{-}P(CH)P^{NMe}\text{-}iPr)(CO)_2]^+$ to oxygen or TEMPO to yield the paramagnetic Co^{II} PCP complex $[Co(PCP^{NMe}\text{-}iPr)(CO)_2]^+$. Finally, replacement of one CO ligand in $[Co(\kappa^3P,CH,P\text{-}P(CH)P^{NMe}\text{-}iPr)(CO)_2]^+$ by CNtBu promotes the rapid oxidative addition of the agostic η^2-C$_{aryl}$–H bond to give two isomeric hydride complexes of the type $[Co(PCP^{NMe}\text{-}iPr)(CNtBu)(CO)(H)]^+$.*

The selective activation and breaking of strong C–H bonds by transition metal complexes is of great importance in chemistry. Much research is devoted to fundamentally understanding these processes, which are key steps in many organic and organometallic reactions. In recent years, catalytic C–H bond activation reactions in particular have emerged as a powerful synthetic tool in organic synthesis.[1] There are well-established mechanistic pathways for C–H bond activation reported over the years, including σ-bond metathesis in early transition metal complexes, electrophilic activation in electron-deficient late transition metal complexes, or Lewis-base-assisted metalation.[2] Oxidative addition, which leads to alkyl or aryl hydride complexes, is the typical pathway for electron-rich late transition metals. This process is associated with a formal two-electron oxidation of the metal center. Oxidative addition requires apparently pre-coordination of the C–H bond, that is, the formation of an agostic intermediate or, at least, transition state.[3,4] In this respect, intramolecular and directed C–H activation reactions of Ru, Rh, and Ir PCP pincer complexes led to the formation of stable complexes that contain η^2-C-H agostic arene bonds.[5–11] Agostic square-planar Rh^I pincer complexes reported by Milstein and co-workers are particularly intriguing.[5] These four-coordinate species were unable to cleave the C–H bond and no oxidative addition to form Rh^{III} hydride complexes took place. However, addition of CO, despite of being a weak σ-donor, sufficiently increased the electron density at the metal center and triggered the oxidative addition process (Scheme 1). Based on DFT calculations, the aromatic C–H cyclometalation process was suggested to procced through an elusive agostic-like trigonal bipyramidal dicarbonyl Rh^I intermediate.



Scheme 1. Reaction pathway for the CO induced agostic/aryl hydride equilibrium of rhodium PCP pincer complexes proceeding through a postulated agostic dicarbonyl species.

Herein, we report the synthesis and reactivity of a five-coordinate Co^I PCP pincer complex which features an agostic η^2-C–H arene bond. This is the first agostic pincer complex of a non-precious transition metal, and underlines the strikingly different coordination chemistry of low-spin Co^I and Rh^I complexes. The first typically favor five-coordinate square pyramidal or trigonal bipyramidal geometries,[12] while the latter favor four-coordinate square planar arrangements. Accordingly, the key complex described here may be viewed as a missing link on the pathway to Rh^{III} hydride complexes (Scheme 1).

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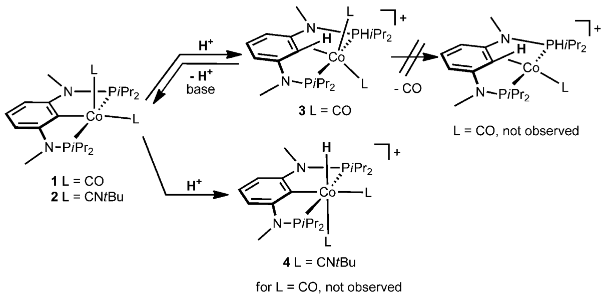
Supporting information for this article, including complete crystallographic data, experimental details of the synthesis of all complexes including ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectra, computational details, technical details in CIF format for **2**, **3**, and **5**, and ORCID(s) from the author(s) are available on the WWW under http://dx.doi.org/10.1002/anie.201510145.



Scheme 2. Synthesis of **3** and **4** upon reaction of **1** and **2**, respectively, with $HBF_4{\cdot}Et_2O$ in CH_2Cl_2 and THF: ligand vs. metal protonation.

Protonation of [Co(PCP^{NMe}-*i*Pr)(CO)$_2$] (**1**)[13] with $HBF_4{\cdot}Et_2O$ leads to the formation of the cationic Co^{I} complex [Co(κ^3*P*,*CH*,*P*-P(CH)P^{NMe}-*i*Pr)(CO)$_2$]$^+$ (**3**) in 94 % isolated yield (Scheme 2). Interestingly, this complex features not only an η^2-C$_{aryl}$−H agostic bond, but also contains two CO ligands, which contrasts with the behavior of related Rh complexes where exclusively square-planar mono CO complexes are formed (Scheme 1).

There was no evidence for the formation of the monocarbonyl complex [Co(κ^3*P*,*CH*,*P*-P(CH)P^{NMe}-*i*Pr)(CO)]$^+$ or the Co^{III} hydride complex [Co(PCP^{NMe}-*i*Pr)(CO)$_2$(H)]$^+$. Complex **3** was fully characterized by a combination of ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectroscopy, IR, ESI MS, elemental analysis, and X-ray crystallography. An important feature of the ^{1}H NMR spectrum is the high field shift of the proton attached to the *ipso*-carbon, giving rise to a triplet at 2.23 ppm ($^4J_{HP} = 7.5$ Hz). In the ^{13}C-{^{1}H} NMR spectrum, the *ipso*-carbon atom exhibits a signal at 67.0 ppm (105.3 ppm in the free PCP ligand; Figure 1), the two CO ligands give rise to two low-field resonances as poorly resolved triplets centered at 197.9 and 197.5 ppm. The relatively low $^1J_{HC}$ coupling constant of 102.0 Hz, as compared to 160.5 and 163.5 Hz for the other aromatic C−H bonds, is also characteristic for a strong C−H metal interaction.[7–9] Complex **3** exhibits two bands at 1950 and 2009 cm^{-1} in the IR spectrum for the mutually *cis* CO ligands, assignable to the symmetric and asymmetric CO stretching frequencies, respectively (compare 1906 and 1963 cm^{-1} in the more electron-rich complex **1**).

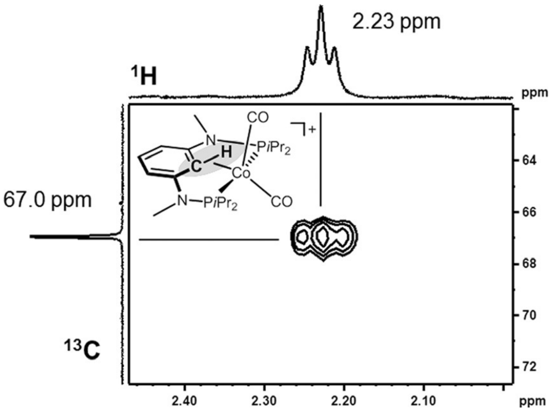


Figure 1. Section of the ^{1}H-^{13}C HSQC spectrum of **3** in CD_2Cl_2 exhibiting a cross-peak between the agostic H1 and C1 atoms.

A structural view of **3** is depicted in Figure 2. The overall geometry about the cobalt center is best described as distorted trigonal bipyramidal, where the two carbonyl ligands and the agostic η^2-C$_{aryl}$-H bond define the equatorial plane and the phosphine moieties the axial positions. The bond between the *ipso*-carbon and the Co atom is extremely long (2.2197(6) Å) relative to regular cobalt–carbon σ-bonds. For instance, the Co−C$_{ipso}$ bond lengths in the Co^{I} and Co^{II} PCP complexes [Co(PCP^{NMe}-*i*Pr)(CO)$_2$] (**1**) and [Co(PCP^{NMe}-*i*Pr)(CO)$_2$]$^+$ (**5**) are substantially shorter: 1.998(2) and 1.953(2) Å, respectively. The H(1) atom (which was located in difference Fourier maps and refined freely) strongly interacts with the cobalt center (1.72(2) Å), which was also evident from the ^{1}H NMR spectrum of **3**. It is noteworthy that this hydrogen is severely removed from the aromatic plane by approximately 35° (in related Ru, Rh, and Os complexes, this angle is in the range of 14–30°).[5,7,10,14] The C1−H1 bond length of 1.05(3) Å is in the range observed in X-ray diffraction measurements for unactivated hydrocarbons (for example, 1.08 Å in C_6H_6).

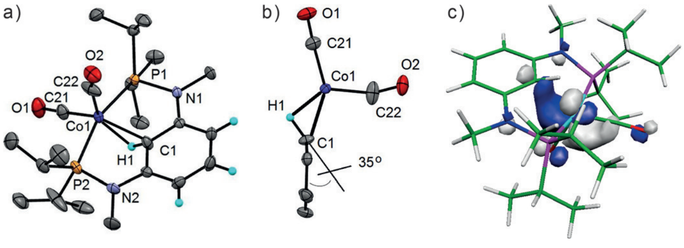
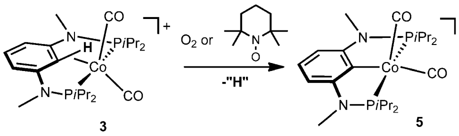


Figure 2. a) Structural view of **3** showing 50 % thermal ellipsoids (most H atoms and BF_4^- counterion omitted for clarity). b) Positioning of H1 in relation to the Co center and to the benzene ring. c) HOMO-2 of complex **3** (1.2 eV below the HOMO).

The nature of the interaction between the C1−H1 bond and the Co atom in complex **3** was investigated by means of DFT/PBE0 calculations. The relevant Wiberg indices (WI)[15] indicate the formation of weak Co−C and Co−H bonds, with WI = 0.17 and 0.05, respectively, suggesting the existence of an agostic C−H···Co bond. As a consequence, there is a clear weakening of the C−H bond, much longer (1.14 Å) and weak (WI = 0.76) than the remaining C$_{aryl}$−H bonds (1.08 Å and WI = 0.90), justifying the proton acidity revealed by complex **3** (see below). Moreover, the HOMO-2 of complex **3** (Figure 2) represents π-back donation from a Co d-orbital to the C−H σ* orbital, being characteristic of an agostic bond and corroborating the experimental results.

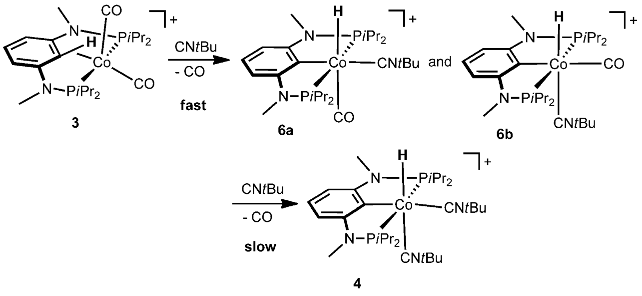
If, on the other hand, [Co(PCP^{NMe}-*i*Pr)(CN*t*Bu)$_2$] (**2**; isocyanides are stronger electron donating ligands than CO)[16,17] is treated with $HBF_4{\cdot}Et_2O$, the metal center is now protonated, exclusively affording the octahedral cationic Co^{III} hydride complex [Co(PCP^{NMe}-*i*Pr)(CN*t*Bu)$_2$(H)]$^+$ (**4**) in 94 % isolated yield (Scheme 2). DFT calculations reveal that **4** is thermodynamically more favorable by 4.7 kcal mol^{-1} as compared to an unobserved agostic complex. The ^{1}H NMR spectrum confirmed the presence of one hydride ligand, which appeared at −13.76 ppm, as a well-resolved triplet with a $^2J_{HP}$ coupling constant of 50.0 Hz. In the ^{13}C{^{1}H} NMR spectrum, the *ipso* carbon atom gives rise to a triplet centered at 101.1 ppm ($J_{HP}=5.6$ Hz). Moreover, in the ESI MS spectrum of **4**, the intact complex [M]$^+$ was observed as a major fragment with *m*/*z* 593.3.

The agostic C−H arene bond in [Co(κ^3*P*,*CH*,*P*-P-(CH)P^{NMe}-*i*Pr)(CO)$_2$]$^+$ (**3**) is activated and can be cleaved in various ways. First, the agostic proton is comparatively acidic, and thus even relatively weak bases, such as pyridine, deprotonate this bond to reform the starting material **1**. Accordingly, protonation of **1** is fully reversible (Scheme 2). Second, cleavage of the agostic C−H arene bond is also achieved upon exposure of **3** to air (oxygen) or TEMPO, which results in the immediate formation of the cationic paramagnetic Co^{II} PCP complex [Co(PCP^{NMe}-*i*Pr)(CO)$_2$]$^+$ (**5**; Scheme 3).[14] This process involves hydrogen abstraction with concomitant oxidation of the metal center from Co^I to Co^{II}. The fate of the hydrogen atom is unclear as yet.



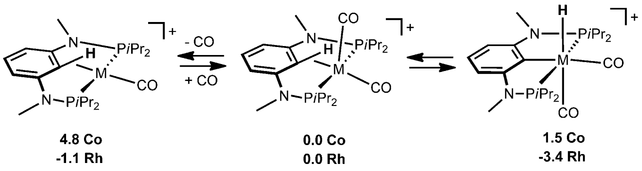
Scheme 3. Reaction of **3** with oxygen or TEMPO in CH_2Cl_2.

Finally, replacement of one CO ligand in **3** by CN*t*Bu actually promotes the rapid oxidative addition of the agostic C−H arene bond (Scheme 4). Treatment of **3** in CD_2Cl_2 with 2.4 equivs of CN*t*Bu results in the quantitative formation of two isomeric Co^{III} hydride complexes of the type [Co(PCP^{NMe}-*i*Pr)(CN*t*Bu)(CO)(H)]$^+$ (**6a**, **6b**) in a roughly 1:2 ratio together with small amounts of [Co(PCP^{NMe}-*i*Pr)-(CN*t*Bu)$_2$(H)]$^+$ (**4**). The hydride ligands of the two isomers **6a** (hydride *trans* to CO) and **6b** (hydride *trans* to CN*t*Bu) exhibit well-resolved triplet resonances at −10.81 and −12.86 ppm with $^2J_{HP}$ coupling constants of 40.7 and 44.9 Hz, respectively. After about 16 h, **6a** and **6b** were quantitatively converted to **4**.



Scheme 4. Stepwise replacement of CO from **3** upon addition of CN*t*Bu in CD_2Cl_2.

The free energy balances calculated for the CO addition reactions reproduce the differences observed for the Co and the Rh complexes (Scheme 5). While for the Co species the trigonal bipyramidal complex **3** is the most stable one, in the case of Rh, both CO loss with formation of the square planar complex, as well as C−H oxidative addition, are thermodynamic favorable processes.



Scheme 5. Thermodynamic comparisons between Co and Rh complexes based on DFT/PBE0 calculations (Free energies in kcal mol^{-1}).

In conclusion, we describe the synthesis and reactivity of the first Co^I pincer complex [Co(κ^3*P*,*CH*,*P*-P(CH)P^{NMe}-*i*Pr)-(CO)$_2$]$^+$ featuring an agostic η^2-C$_{aryl}$−H bond. In contrast to related Rh^I agostic pincer complexes, this complex is five-coordinate and adopts trigonal bipyramidal geometry. Because the CO ligands are not sufficiently electron-rich to promote an oxidative addition of the C−H bond, a Co^{III} hydride complex is not formed. A Co^{III} hydride complex [Co(PCP^{NMe}-*i*Pr)(CNtBu)$_2$(H)]$^+$ was obtained upon protonation of [Co(PCP^{NMe}-*i*Pr)(CNtBu)$_2$]. The agostic C−H arene bond can be cleaved easily by deprotonation, or radical abstraction with oxygen or TEMPO, to afford the paramagnetic Co^{II} PCP complex [Co(PCP^{NMe}-*i*Pr)(CO)$_2$]$^+$, or by isocyanide-promoted oxidative addition to give Co^{III} PCP hydride complexes [Co(PCP^{NMe}-*i*Pr)(CN*t*Bu)(CO)(H)]$^+$. DFT calculations support the existence of the agostic bond in complex [Co(κ^3*P*,*CH*,*P*-P(CH)P^{NMe}-*i*Pr)(CO)$_2$]$^+$ and corroborate the differences observed between the Co and the Rh species.

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[1] For recent reviews on C−H activation and functionalization, see, a) C. Jia, T. Kitamura, Y. Fujiwara, *Acc. Chem. Res.* **2001**, *34*, 633–639; b) V. Ritleng, C. Sirlin, M. Pfeffer, *Chem. Rev.* **2002**, *102*, 1731–1770; c) D. A. Colby, R. G. Bergman, J. A. Ellman, *Chem. Rev.* **2010**, *110*, 624–655; d) P. B. Arockiam, C. Bruneau, P. H. Dixneuf, *Chem. Rev.* **2012**, *112*, 5879–5918; e) J. C. Lewis,

R. G. Bergman, J. A. Ellman, *Acc. Chem. Res.* **2008**, *41*, 1013–1025; f) S. Gaillard, C. S. J. Cazin, S. P. Nolan, *Acc. Chem. Res.* **2012**, *45*, 778–787; g) B. Li, P. H. Dixneuf, *Chem. Soc. Rev.* **2013**, *42*, 5744–5767; h) J. Wencel-Delord, T. Dröge, F. Liu, F. Glorius, *Chem. Soc. Rev.* **2011**, *40*, 4740–4761.

[2] a) A. E. Shilov, G. B. Shul′pin, *Chem. Rev.* **1997**, *97*, 2879–2932; b) J. A. Labinger, J. E. Bercaw, *Nature* **2002**, *417*, 507–514; c) S. Sakaki, *Top. Organomet. Chem.* **2005**, *12*, 31–78.

[3] For the central role of agostic interactions in C–H activations, see, a) C. Hall, R. N. Perutz, *Chem. Rev.* **1996**, *96*, 3125–3146; b) R. H. Crabtree, *J. Organomet. Chem.* **2004**, *689*, 4083–4091; c) B. Rybtchinski, R. Cohen, Y. Ben-David, J. M. L. Martin, D. Milstein, *J. Am. Chem. Soc.* **2003**, *125*, 11041–11050; d) W. D. Jones, *Inorg. Chem.* **2005**, *44*, 4475–4484; e) W. H. Bernskoetter, C. K. Schauer, K. I. Goldberg, M. Brookhart, *Science* **2009**, *326*, 553–556.

[4] C. Lepetit, J. Poater, M. E. Alikhani, B. Silvi, Y. Canac, J. Contreras-García, M. Sola, R. Chauvin, *Inorg. Chem.* **2015**, *54*, 2960–2969.

[5] a) A. Vigalok, O. Uzan, L. J. W. Shimon, Y. Ben-David, J. L. Martin, D. Milstein, *J. Am. Chem. Soc.* **1998**, *120*, 12539–12544; b) A. Vigalok, B. Rybtchinski, L. J. W. Shimon, Y. Ben-David, D. Milstein, *Organometallics* **1999**, *18*, 895–905; c) M. Montag, L. Schwartsburd, R. Cohen, G. Leitus, Y. Ben-David, J. M. L. Martin, D. Milstein, *Angew. Chem. Int. Ed.* **2007**, *46*, 1901–1904; *Angew. Chem.* **2007**, *119*, 1933–1936; d) C. M. Frech, L. J. W. Shimon, D. Milstein, *Organometallics* **2009**, *28*, 1900–1908; e) M. Montag, I. Efremenko, R. Cohen, L. J. W. Shimon, G. Leitus, Y. Diskin-Posner, Y. Ben-David, H. Salem, J. M. L. Martin, D. Milstein, *Chem. Eur. J.* **2010**, *16*, 328–353.

[6] A. C. Albeniz, G. Schulte, R. H. Crabtree, *Organometallics* **1992**, *11*, 242–249.

[7] a) P. Dani, T. Karlen, R. A. Gossage, W. J. J. Smeets, A. L. Spek, G. van Koten, *J. Am. Chem. Soc.* **1997**, *119*, 11317–11318; b) P. Dani, M. A. M. Toorneman, G. P. M. van Klink, G. van Koten, *Organometallics* **2000**, *19*, 5287–5296.

[8] M. A. McLoughlin, R. J. Flesher, W. C. Kaska, H. A. Mayer, *Organometallics* **1994**, *13*, 3816–3822.

[9] M. E. van der Boom, M. A. Iron, O. Atasoylu, L. J. W. Shimon, H. Rozenberg, Y. Ben-David, L. Konstantinovski, J. M. L. Martin, D. Milstein, *Inorg. Chim. Acta* **2004**, *357*, 1854–1864.

[10] D. G. Gusev, M. Madott, F. M. Dolgushin, K. A. Lyssenko, M. Y. Antipin, *Organometallics* **2000**, *19*, 1734–1739.

[11] C. Barthes, C. Lepetit, Y. Canac, C. Duhayon, D. Zargarian, R. Chauvin, *Inorg. Chem.* **2013**, *52*, 48–58.

[12] Diamagnetic square-planar d^8-complexes of Co$^{\mathrm{I}}$ are rare in comparison to Rh$^{\mathrm{I}}$ and Ir$^{\mathrm{I}}$ species. In most cases, Co$^{\mathrm{I}}$ species tend to slip away to the high-spin state or to higher oxidation states like Co$^{\mathrm{II}}$ or Co$^{\mathrm{III}}$, for examples see: a) Z. Mo, Y. Li, H. K. Lee, L. Deng, *Organometallics* **2011**, *30*, 4687–4694; b) Q. Knijnenburg, D. Hetterscheid, T. M. Kooistra, P. H. M. Budzelaar, *Eur. J. Inorg. Chem.* **2004**, 1204–1211.

[13] S. Murugesan, B. Stöger, M. D. Carvalho, L. P. Ferreira, E. Pittenauer, G. Allmaier, L. F. Veiros, K. Kirchner, *Organometallics* **2014**, *33*, 6132–6140.

[14] R. Castro-Rodrigo, M. A. Esteruelas, A. M. Lopez, E. Oñate, *Organometallics* **2008**, *27*, 3547–3555.

[15] a) K. B. Wiberg, *Tetrahedron* **1968**, *24*, 1083–1096; b) Wiberg indices are electronic parameters related with the electron density between two atoms, which serve as bond strength indicators. They can be obtained from a Natural Population Analysis.

[16] This complex was prepared by treatment of [Co(PCP$^{\mathrm{Me}}$-*i*Pr)(η^2-BH$_4$)] (ref. [17]) with 2 equivs of CN*t*Bu.

[17] S. Murugesan, B. Stöger, L. F. Veiros, K. Kirchner, *Organometallics* **2015**, *34*, 1364–1372.

[18] CCDC 1049854, 1049856, and 1049857 contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

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