ChemComm

RSCPublishing

COMMUNICATION

View Article Online
View Journal | View Issue

Formal loss of an H radical by a cobalt complex *via* metal–ligand cooperation†

Cite this: *Chem. Commun.*, 2013, **49**, 2771

Received 18th December 2012,
Accepted 15th February 2013

DOI: 10.1039/c3cc39049g

www.rsc.org/chemcomm

Eugene Khaskin,[a] Yael Diskin-Posner,[b] Lev Weiner,[b] Gregory Leitus[b] and David Milstein*[a]

A (PNP)Co(I)methyl diamagnetic complex formally loses an H atom from the pincer ligand, exhibiting a long-range metal–ligand cooperation in what may be considered as an unusual example of 'C–H cleavage'. Spectroscopic data indicate that the product is a neutral Co(I) complex with a radical delocalized in the ligand backbone.

Pincer cobalt complexes have been extensively studied due to their unique catalytic and electronic properties. Brookhart[1] and Gibson[2] first noted the high catalytic activities of imine NNN pincer complexes of iron and cobalt in ethylene polymerization. For the Co(II) dichloride catalysts, it was later suggested that a Co(I) intermediate generated *in situ* was responsible for the polymerization activity.[3] The isolation of square planar halide and alkyl Co(I) intermediates engendered a study of their unique electronic properties by Budzelaar.[4] This ligand set is similar to that used by Chirik's group for cobalt complexes for polymerization and structural studies, often differing only in the nature of the imine substituent.[5]

PSiNSiP pincer cobalt complexes were extensively studied by Fryzuk and Caulton with the anionic ligand resulting in Co(II) species when generating mono-alkyl complexes.[6] The three coordinate (PNP)Co(I) synthon reported by Caulton is a high-spin triplet.[6b,c] The POCOP ligand, reported to be stabilizing a Co dihydride complex by Heinekey, presents a very similar electronic environment to the metal.[7] Danoupolos reported a neutral Co(I) carbene pincer complex without noting unusual reactivity.[8] The aforementioned ligand systems are summarized in Fig. 1.

Curiously, neutral pincer phosphine donor ligands, such as the PNP platform used in this report, are not widely reported in cobalt chemistry beyond studies on simple Co dihalide adducts.[9] However, neutral Co(I) alkyls could have a role as catalysts in hydrogenation of CO$_2$, as suggested by a recent DFT study,[10] and we planned to prepare such compounds and explore their properties.

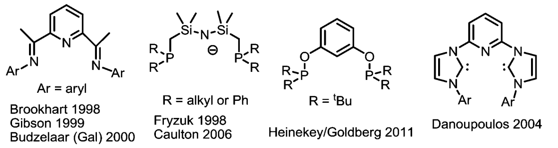
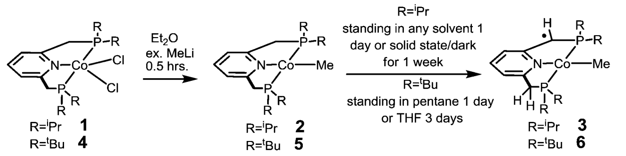


Fig. 1 Ligand platforms relevant to the current study.

Reports by the groups of Fryzuk and Danoupoulos,[6a,8] using an anionic PNP ligand to generate Co(II) alkyl complexes, as well as a report by the groups of Erker and Bazan,[11] suggested that Co(I) alkyls might be generated from LCo(II)Cl$_2$ by the addition of excess Grignard or alkyl lithium reagent. Indeed, reaction of the Co(II) complex **1**, obtained by reaction of CoCl$_2$ with the iPr-PNP ligand (see ESI†), with an excess of MeLi in diethylether generated the diamagnetic Co(I)Me species **2** with no deprotonation of the benzylic protons being observed. The complex was isolated as a dark brown solid and characterized by ^{1}H NMR (Scheme 1).

Complex **2** was not stable in C$_6$D$_6$, transforming into dark brown paramagnetic complex **3** (Scheme 1) whose ^{1}H NMR exhibited a few broad peaks in the 40–60 ppm region, as well as two large, very broad peaks from 12–16 ppm, probably ligand CH$_3$ groups, and signals in the upfield regions whose number is consistent with an unsymmetrical complex. Pure crystals of **3** were obtained from a pentane solution of **2**. An X-ray diffraction study, in which all hydrogen atoms were located, unambiguously shows a square planar, asymmetric complex that is missing one hydrogen atom on one of the arms (Fig. 2).

The structure of **3** exhibits a short C6–C7 bond (1.415(4) Å) of the pyridine arm with only one hydrogen atom, which is typical of a double bond. This suggests conjugation of the ring, which



Scheme 1 Synthesis of complexes **2–3** and **5–6**.

---

[a] *Department of Organic Chemistry, Weizmann Institute of Science, Rehovot, Israel. E-mail: david.milstein@weizmann.ac.il; Fax: +972-8-934-4142; Tel: +972-8-934-2599*

[b] *Department of Chemical Research Support, Weizmann Institute of Science, Rehovot, Israel*

† Electronic supplementary information (ESI) available: Synthesis of all complexes, experimental details and DFT study. CCDC 916115–916117. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3cc39049g

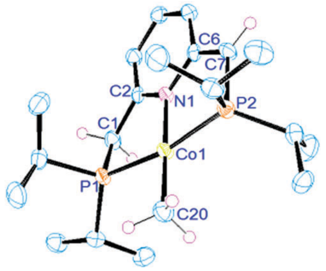
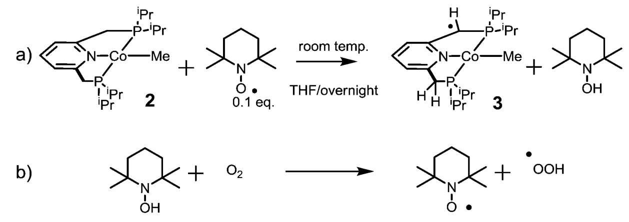


Fig. 2 Selected bond lengths (Å) Co1-C20, 1.975(3); Co1-N1, 1.949(3); Co1-P1, 2.1732(9); Co1-P2, 2.1912(9); C1-C2, 1.499(4); C7-C6, 1.415(3). Selected angles (degrees) P1-Co1-P2, 169.55(4); N1-Co1-C20, 179.27(12). One of the two independent molecules in an asymmetric unit. ORTEP diagram of **3** (50% ellipsoid probability level).

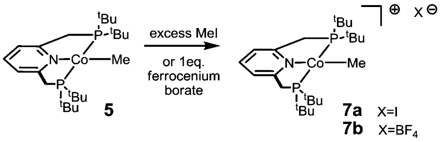
remains planar and aromatic judging from the short bond lengths. The plane made by C6–C7–P2 and the C7 hydrogen atom indicates sp^2 conjugation of the central carbon. The other arm with two hydrogens has a C2–C1 bond length of 1.499 Å, considerably longer than C6–C7. Evans magnetic measurements of **3** at several different concentrations in C_6D_6 gave an average value of μ_{eff} of ~2.2. The EPR signal of complex **3** by itself is reminiscent of an organic radical's spectrum that is visible at room temperature ($g = 2.0046$) (see ESI† Fig. S20). The structural and spectroscopic evidence suggests one unpaired electron for the complex that is mostly delocalized on the ligand, although the nitrogen triplet remains unresolved. The only structural difference between **2** and **3** is one hydrogen atom (both are neutral species that are very soluble in non-polar organic solvents). To the best of our knowledge, radical formation at ambient temperatures using an organometallic species, involving bond scission at a site remote from the metal center, has not been reported before. Importantly, the yield of complex **3** was above 80%, ruling out a disproportionation pathway.

Intriguingly, complex **2** transforms into **3** also in the solid state, albeit at a slower rate than in solution. When samples of solid **3** were intermittently measured using ^1H NMR in C_6D_6 over a period of several days, a steady transformation to **3** was observed. By the end of three days, mostly **3** was present, and only a small amount of **2** remained. An experiment in the dark showed no qualitative difference in the rate of the transformation.

The transformation of **2** to **3** was conveniently followed by EPR in the presence of a TEMPO (2,2,6,6-tetramethylpiperidine-1-oxy) radical using a 10-fold molar excess solution of **2** in THF (Scheme 2). In the beginning a strong TEMPO signal was clearly seen, and it slowly degraded over time as confirmed by a series of five-minute measurements. Eventually, the signal was low enough to allow observation of the signal of complex **3** as well, and the TEMPO triplet completely disappeared after an overnight reaction. Exposing the sample to air regenerated the strong TEMPO triplet by presumably forming a hydroperoxy radical (ESI† Fig. S20; see Scheme 2).[12]



Scheme 2 (a) Transformation of TEMPO to an EPR-silent compound. (b) Regeneration of TEMPO with oxygen.



Scheme 3 Synthesis of **7** by $1e^-$ oxidation of **5**.

The ^{t}Bu-PNP analogue of complex **1** was prepared by reaction of the ^{t}Bu-PNP ligand with $CoCl_2$, resulting in the purple, crystalline complex (^{t}Bu-PNP)$CoCl_2$ **4**. Adding an excess of MeLi to **4** in benzene or ether and stirring for several hours resulted in formation of the diamagnetic, dark black complex **5** whose NMR characteristics mirrored those of **2**. Complex **5** was stable in the solid state or in benzene, but it exhibited a slow interconversion to **6** in THF, and a rapid interconversion to **6** in pentane (see Scheme 1). Unlike complex **3**, good-quality crystals of **6** could not be isolated. The paramagnetic ^1H NMR of **6** was closely analogous to that of **3**, with signals in the same areas and one signal missing in the far downfield region, entirely consistent with a ^{t}Bu for ^{i}Pr substitution.

Reaction of complex **5** with an excess of MeI was slightly different from that observed for related Co species.[4d,5a] Instead of oxidative addition, a radical process resulting in oxidation of the metal center to give the Co(II) complex **7a** took place (Scheme 3 and Fig. 3). The reaction is instantaneous at room temperature, resulting in rapid color change from dark black to green. X-ray structural determination of crystals obtained from a benzene solution exhibits a square planar geometry with a non-coordinating iodide anion. We believe that electron donation from **5** to MeI leads to the radical anion $[\mathrm{MeI}]^{-\bullet}$ followed by iodide expulsion and generation of a Me radical. The analogous green complex **7b** was obtained by electron transfer to ferrocenium borate and was also characterized using X-ray spectroscopy. Both **7b** and **7a** have exactly the same geometry with fully protonated ligand arms. If cationic **7** is assumed to be isostructural with complexes **2** and **5**, comparing bond lengths between the structure of **7** and **3** allows for further conclusions on the radical nature of **3**. As mentioned above, the aromaticity in the central pyridine ring is maintained, however the bond lengths are slightly elongated in **3** compared to complexes **7**, consistent with delocalization of an extra unpaired electron in an anti-bonding orbital and suggesting that after the loss of an H atom, the lone electron density is not confined to the ligand arm.

We turned our attention to determining the fate of the H atom that is lost from the ligand arm. Other metal complexes, such as

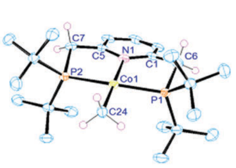
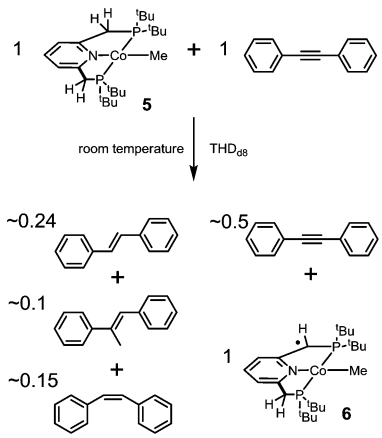


Fig. 3 Selected bond lengths (Å) Co1-C24, 2.008(3); Co1-N1, 2.008(2); Co1-P1, 2.2274(8); Co1-P2, 2.2349(7); C1-C6, 1.503(4); C7-C5, 1.499(4). Selected angles (degrees) P1-Co1-P2, 169.52(3); C24-Co1-N1, 178.59(11). ORTEP diagram of **7a** (50% ellipsoid probability level).

n-Bu_3SnH, are known to be potent sources of H radicals. However, homolytic C–H cleavage to give an H radical at room temperature is unlikely (see the DFT section in ESI†). H_2 was not detected by ^1H NMR when carrying out the syntheses of **3** and **6** in closed tubes, or by GC/TCD. In addition, the known H_2 scavenger $(PEt_3)_3IrCl$[13] remained unchanged during the transformation, even when present in the same reaction mixture. Complexes **2** and **5** also decompose rapidly; **3** and **6** slowly, upon addition of H_2 to undetermined paramagnetic species. Thus, the presence of H_2 during a solution reaction is unlikely. The products are obtained in high yield (>80% for complex **3**), ruling out a disproportionation pathway but not an intermolecular one even in the solid state, both however being disfavored by sterics. In addition, the dramatically increased reaction rate in aliphatic solvents argues for a significant solvent role in the abstraction of the putative H radical.

It was of interest to abstract the (formally) H radical from the complex by use of an appropriate substrate. The reaction with olefins and aliphatic alkynes was unsuccessful. However, when diphenylacetylene (dpa) was added to samples of **2** and **5** in THF_{d8} or $dioxane_{d8}$, stilbene products were obtained. Upon a slow, room temperature transformation of **5** in the presence of an equivalent amount of dpa, ~50% conversion of dpa took place to yield a 1 : 1 mixture of *cis*-stilbene and *trans*-stilbene, in addition to a small amount of α-methyl-stilbene[4b] (see ESI†). Half the dpa remained unreacted after two days, with no further change after one week. The presence of *cis*-stilbene may indicate a metal-complex mediated role in H radical transfer, perhaps *via* coordination of a radical organic intermediate. The dpa → stilbene experiment serves to confirm the transformation and its stoichiometry (Scheme 4). In all reactions, the stilbene products were *not deuterated*; hence the origin of H atoms was the metal complex and not the solvent.

In conclusion, we observed C–H bond cleavage at room temperature at a site remote from the metal, mediated by a cobalt center. This transformation should be considered in the chemistry of cobalt based enzymes and complexes, where a remotely formed radical can play a role in substrate transformations. A recent report on a ytterbium complex that loses H atoms remotely shows that in contrast, that reaction involves an intermediate dimerization and the production of H_2 with the organometallic product having a metal centered radical.[14]



Scheme 4 Capture of an H radical by dpa.

The neutral complexes formed in the current report *via* homolytic cleavage of an arm CH bond can be compared to the heterolytic cleavage of pincer complexes of Ru and Rh reported earlier by our group, where full dearomatization of the central pyridine ring in favor of a 6π conjugated system was observed.[15] Crystal structure evidence points to an intermediate case for complex **3**, where aromatization of the pyridine ring is still evident, but the unpaired electron is delocalized on the arm and throughout the ring.

This research was supported by the European Research Council under the FP7 framework (ERC No. 246837), the Minerva Foundation, and the Kimmel Center for Molecular Design. D.M. is the Israel Matz Professor of Organic Chemistry.

Notes and references

1 B. L. Small, M. Brookhart and A. M. A. Bennett, *J. Am. Chem. Soc.*, 1998, **120**, 4049–4050.
2 (*a*) G. J. P. Britovsek, V. C. Gibson, B. S. Kimberley, P. J. Maddox, S. J. McTavish, G. A. Solan, A. J. P. White and D. J. Williams, *Chem. Commun.*, 1998, 849–850; (*b*) G. J. P. Britovsek, M. Bruce, V. C. Gibson, B. S. Kimberley, P. J. Maddox, S. Mastoianni, S. J. McTavish, C. Redshaw, G. A. Solan, S. Stroemberg, A. J. P. White and D. J. Williams, *J. Am. Chem. Soc.*, 1999, **121**, 8728–8740; (*c*) V. C. Gibson and G. A. Solan, *Top. Organomet. Chem. "Iron-Based and Cobalt-Based Olefin Polymerisation Catalysts"*, Springer-Verlag Berlin, Heidelberg, 2008.
3 (*a*) T. M. Kooistra, Q. Knijnenburg, J. M. M. Smits, A. D. Horton, P. H. M. Budzelaar and A. W. Gal, *Angew. Chem., Int. Ed.*, 2001, **40**, 4719–4722; (*b*) K. P. Tellman, M. J. Humphries, H. S. Rzepa and V. C. Gibson, *Organometallics*, 2004, **23**, 5503–5513.
4 (*a*) Q. Knijnenburg, D. Hetterscheid, T. M. Kooistra and P. H. M. Budzelaar, *Eur. J. Inorg. Chem.*, 2004, 1204–1211; (*b*) Q. Knijnenburg, S. Gambarotta and P. H. M. Budzelaar, *Dalton Trans.*, 2006, 5442–5448; (*c*) D. Zhu and P. H. M. Budzelaar, *Organometallics*, 2008, **27**, 2699–2705; (*d*) D. Zhu, I. Thapa, I. Korobkov, S. Gambarotta and P. H. M. Budzelaar, *Inorg. Chem.*, 2011, **50**, 9879–9887; (*e*) D. Zhu, I. Korobkov and P. H. M. Budzelaar, *Organometallics*, 2012, **31**, 3958–3971.
5 (*a*) A. C. Bowman, C. Milsmann, C. C. H. Atienza, E. Lobkovsky, K. Wieghardt and P. J. Chirik, *J. Am. Chem. Soc.*, 2010, **132**, 1676–1684; (*b*) C. C. H. Atienza, A. C. Bowman, E. Lobkovsky and P. J. Chirik, *J. Am. Chem. Soc.*, 2010, **132**, 16343–16345; (*c*) A. C. Bowman, C. Milsmann, E. Bill, E. Lobkovsky, T. Weyhermueller, K. Wieghardt and P. J. Chirik, *Inorg. Chem.*, 2010, **49**, 6110–6123; (*d*) S. Monfette, Z. R. Turner, S. P. Semproni and P. J. Chirik, *J. Am. Chem. Soc.*, 2012, **134**, 4561–4564.
6 (*a*) M. D. Fryzuk, D. B. Leznoff, R. C. Thompson and S. J. Rettig, *J. Am. Chem. Soc.*, 1998, **120**, 10126–10135; (*b*) M. J. Ingleson, M. Pink, H. Fan and K. G. Caulton, *Inorg. Chem.*, 2007, **46**, 10321–10334; (*c*) M. J. Ingleson, M. Pink and K. G. Caulton, *J. Am. Chem. Soc.*, 2006, **128**, 4248–4254; (*d*) M. J. Ingleson, M. Pink, H. Fan and K. G. Caulton, *J. Am. Chem. Soc.*, 2008, **130**, 4262–4276.
7 T. J. Hebden, A. J. St. John, D. G. Gusev, W. Kaminsky, K. I. Goldberg and D. M. Heinekey, *Angew. Chem., Int. Ed.*, 2011, **50**, 1873–1876.
8 A. A. Danopoulos, J. A. Wright, W. B. Motherwell and S. Ellwood, *Organometallics*, 2004, **23**, 4807–4810.
9 For examples see: (*a*) Q. Dong, M. J. Rose, W.-Y. Wong and H. B. Gray, *Inorg. Chem.*, 2011, **50**, 10213–10224; (*b*) K. Abdur-Rashid, G. Todd, C.-W. Tsang, C. Xuanhua, G. Rognwei, J. Wenli, A. Dino and C. Sui-Seng, *WO*2008141439, 2008.
10 X. Yang, *ACS Catal.*, 2011, **1**, 849–854.
11 N. Kleigrewe, W. Steffen, T. Bloemker, G. Kehr, R. Froehlich, B. Wibbeling, G. Erker, J.-C. Wasilke, G. Wu and G. C. Bazan, *J. Am. Chem. Soc.*, 2005, **127**, 13955–13968.
12 G. I. Shchukin and I. A. Grigor'ev, in *Imidazoline Nitroxides*, ed. L. B. Volodarsky, CRC Press, Boca Raton, FL, vol. I, Ch. 6, 1988.
13 O. Blum and D. Milstein, *J. Am. Chem. Soc.*, 1995, **117**, 4582–4594.
14 G. Nocton, C. H. Booth, L. Maron and R. A. Andersen, *Organometallics*, 2013, ASAP.
15 For some examples see: (*a*) E. Khaskin, M. A. Iron, L. J. W. Shimon, J. Zhang and D. Milstein, *J. Am. Chem. Soc.*, 2010, **132**, 8542–8543; (*b*) M. Feller, Y. Diskin-Posner, L. J. W. Shimon, E. Ben-Ari and D. Milstein, *Organometallics*, 2012, **31**, 4083–4101.