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Binuclear Oxidative Addition of Aryl Halides

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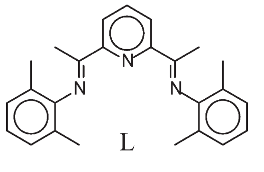
Summary: Reaction of $LCoCH_2SiMe_3$ *(L = 2,6-bis[2,6-dimethylphenyliminoethyl]pyridine) with* H_2 *produces* $LCo(N_2)$*, presumably via intermediate LCoH. Reaction of* $LCo(N_2)$ *(prepared in this way or via reaction of* $LCoCl_2$ *with Na/Hg) with aryl halides ArX (X = Cl, Br, I) produces LCoAr and LCoX in a ratio depending on the nature of Ar and X. For X = Cl, the reaction is slowest but also produces the largest amount of LCoAr. Electron-withdrawing substituents both accelerate the reaction and improve the yield of LCoAr. Computational studies support a radical mechanism for this reaction, involving displacement of* N_2 *to give LCo(XAr) followed by loss of the Ar radical, which then binds to a second Co(0) moiety.*

Oxidative addition of carbon−halogen bonds is one of the fundamental reactions of organometallic compounds; it forms the basis for many applications in organic synthesis. The most common mechanisms of oxidative addition of halides RX are[1] (a) S_N2-like nucleophilic attack by an electron-rich metal center (mostly for alkyl halides); (b) concerted addition via a three-center transition state (mostly for aryl halides); and (c) radical mechanisms (usually for activated alkyl halides). In all of these, the addition product has the halide and organic group bound to the same metal atom, increasing the oxidation state of the metal by 2. Examples of binuclear oxidative addition, in which the R and X groups end up on separate metal centers, are much rarer and mostly involve addition of alkyl halides;[2] the only example involving an aryl halide reported to date seems to be the reaction of 2-I-C_5H_4N with $Co(CN)_5^{3-}$ to give $ICo(CN)_5^{3-}$ and 2-$C_5H_4NCo(CN)_5^{3-}$.[2e,3] We here report net binuclear oxidative addition of aryl chlorides to two molecules of a $Co^{(0)}$ complex, forming a mixture of Co−X and Co−R complexes via what appears to be a free-radical process.


L

Treatment of a solution of $LCoCH_2SiMe_3$[4] in benzene-d_6 under nitrogen with H_2 produced paramagnetic $LCo(N_2)$;[5−7] formation of this complex probably involves LCoH,[8] but we have not observed this intermediate in the ^1H NMR spectra. In addition to $LCo(N_2)$, small amounts of diamagnetic side products (typically 5−10%) are always observed.

Treatment of the dark green solution of $LCo(N_2)$ with ClC_6H_4-4-Me resulted in formation of $LCoC_6H_4$-4-Me and LCoCl in approximately 0.6:1 ratio (Table 1). Separation of these two products proved impossible, but their identities were established by comparison of ^1H NMR data with independently prepared authentic samples. LCoCl was prepared by reduction of $LCoCl_2$ with Na/Hg.[5] $LCoC_6H_4$-4-Me was obtained from $LCoCl_2$ and LiC_6H_4-4-Me (1:2), and its structure was confirmed by a single-crystal X-ray diffraction study (Figure 1); this is the first structurally characterized diiminepyridine cobalt *aryl* complex reported to date.[9]

Conversion and yield of the reaction were determined for the addition of ClC_6H_4-4-CF_3, which is conveniently monitored

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(6) $LCo(N_2)$ prepared from $LCoCl_2$ and Na/Hg[5] undergoes identical subsequent reactions, but we find $LCoCH_2SiMe_3$ to be a more convenient precursor.

(7) The corresponding $L'CoCH_2SiMe_3$ ($L' = 2,6\text{-}[2,6\text{-}{}^iPr_2C_6H_3N{=}CMe]_2C_5H_3N$) also reacts with H_2, but the product $L'CoH$ is fairly stable, can be observed by ^1H NMR, and does not convert efficiently to $L'Co(N_2)$, presumably for steric reasons. See: (a) Tellmann, K. F.; Humphries, M. J.; Rzepa, H. S.; Gibson, V. C. *Organometallics* **2004**, *23*, 5503. (b) Knijnenburg, Q.; Horton, A. D.; van der Heijden, H.; Kooistra, T. M.; Hetterscheid, D. G. H.; Smits, J. M. M.; de Bruin, B.; Budzelaar, P. H. M.; Gal, A. W. *J. Mol. Catal. A* **2005**, *232*, 151.

(8) Treatment of $LCoCH_2SiMe_3$ with H_2 in the presence of $PhC{\equiv}CPh$ produces a diamagnetic species identified as $LCoCPh{=}CHPh$ on the basis of ^1H NMR; see SI for details.

(9) Ir analogue: (a) Nückel, S.; Burger, P. *Angew. Chem. Int. Ed.* **2003**, *42*, 1632. For a related Fe(0) complex, see: (b) Fernandez, I.; Trovitch, R. J.; Lobkovsky, E.; Chirik, P. J. *Organometallics* **2008**, *27*, 109. For Co aryls bearing different ancillary ligands, see e.g.: (c) Yoshimitsu, S.-I.; Hikichi, S.; Akita, M. *Organometallics* **2002**, *21*, 3762, and references therein. (d) Beck, R.; Sun, H.; Li, X.; Klein, H.-F. *Z. Anorg. Allg. Chem.* **2009**, *635*, 99, and references therein. (e) Will, S.; Lex, J.; Vogel, E.; Adamian, V. A.; Caemelbecke, E. V.; Kadish, K. M. *Inorg. Chem.* **1996**, *35*, 5577, and references therein. (f) Lei, H.; Ellis, B. D.; Ni, C.; Grandjean, F.; Long, G. J.; Power, P. P. *Inorg. Chem.* **2008**, *47*, 10205. (g) Theopold, K. H.; Silvestre, J.; Byrne, E. K.; Richeson, D. S. *Organometallics* **1989**, *8*, 2001. (h) Kays, D. L.; Cowley, A. R. *Chem. Commun.* **2007**, 1053.

(10) The partial “loss” of Ar means less than 2 equiv of $LCo(N_2)$ are consumed per mole of ArCl. Most experiments were actually performed with a 1:1 $LCo(N_2)$:ArX ratio (see Table 1) to maximize the amount of LCoAr formed and hence left no unreacted $LCo(N_2)$ (although we verified the final LCoAr:LCoX ratio did not depend on the initial $LCo(N_2)$:ArX ratio). For reactions carried out using a 2:1 $LCo(N_2)$:ArX ratio, quantification of any leftover $LCo(N_2)$ was difficult because of (a) the broad ^1H NMR resonances of this paramagnetic species; (b) the presence of 5−10% diamagnetic side products from the $LCo(N_2)$ synthesis; (c) limited stability of $LCo(N_2)$ in the reaction mixture.

Table 1. Reactions of $LCo(N_2)$ with Organic Halides[a]

entry	halide	[LCoAr]:[LCoX][c]	rxn time[d]
1	IC_6H_5	0.24	seconds
2	BrC_6H_5	0.25	1 min
3	ClC_6H_5	0.59	hours
4	BrC_6H_2-2,4,6-Me_3	≈0	seconds
5	BrC_6H_2-2,4,6-$^tBu_3$	0.27	seconds
6	ClC_6H_3-2,6-Me_2	≈0	days
7	ClC_6H_4-4-COMe	0.91	30 min
8	ClC_6H_4-4-COOMe	0.83	seconds
9	ClC_6H_4-4-CF_3	0.77	seconds
10	ClC_6H_4-4-F	0.40	seconds
11	ClC_6H_3-3,5-$(OMe)_2$	0.59	seconds
12	ClC_6H_4-4-Cl	0.59	seconds
13	ClC_6H_4-4-Me	0.59	hours
14	ClC_6H_4-4-OMe	0.50	hours
15	IMe	0.71[b]	seconds
16	Cl-*n*-C_4H_9	0.13	seconds
17	Br-*n*-C_6H_{13}	0.30[b]	seconds
18	$BrCH_2C_6H_5$	0.14[b]	seconds
19	$ClCH_2C_6H_5$	0.45[b]	minutes
20	2,6-Cl_2−C_5H_3N	1.00	seconds
21	CH_2=CH-*n*-C_6F_{13}	0.59	minutes
22	F-*n*-C_8H_{17}	N.R.	

[a] Reaction conditions: $LCoCH_2SiMe_3$ (14 mg, 27 μmol), 0.4 mL of C_6D_6, 2 mL of H_2 gas, then ArX (27 μmol, 1.0 equiv). [b] Using 14 μmol (0.5 equiv) of RX. [c] From ^1H NMR; estimated error margin ≈ 5%. [d] Qualitative indication.

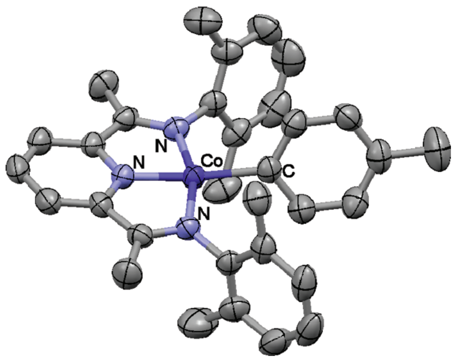
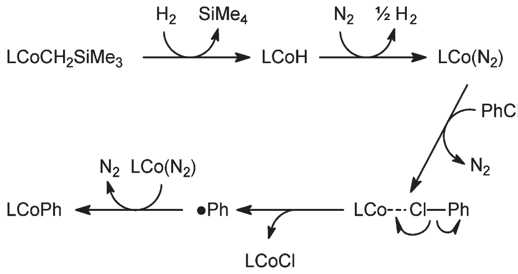


Figure 1. Structure of $LCoC_6H_4$-4-Me (hydrogens omitted for clarity).

by ^1H and ^{19}F NMR spectroscopy. Using a 2:1 $LCo(N_2)$:ArCl ratio, conversion of ArCl was virtually complete (94%). Variation of the amount of ArCl (keeping $[LCo(N_2)]$ constant) did not affect the product ratio LCoAr:LCoCl (0.77 for this aryl; the "lost" Ar groups end up as ArH, detected by ^{19}F NMR, and Ar_2, detected by GC/MS[10]). The oxidative addition was then explored for a variety of halides with different electronic and steric properties (Table 1). Relative amounts of LCoAr and LCoX were determined from the characteristic[11] ^1H resonances for Py H4 (triplet around 10 ppm) and imine Me (singlet around −1 ppm); for details see the SI. The reaction rates of phenyl halides increase in the "normal" order Cl < Br < I (entries 1−3). However, the relative amount of LCoAr formed *decreases* in this order, from 0.59 to 0.24. Electron-withdrawing groups accelerate the reaction (entries 3, 7−9, 20) and also increase the amount of LCoAr formed. Sensitivity to steric factors is not very high: even BrC_6H_2-2,4,6-$^tBu_3$ gave a significant amount of LCoAr (entry 5). However, 2,6-di*methyl*-substituted aryls form very little LCoAr (entries 4, 6).[12]

Scheme 1. Proposed Mechanism for Binuclear Oxidative Addition of ClC_6H_5



We believe these results are best explained by a radical process similar to that shown in Scheme 1 (analogous mechanisms have been proposed for alkyl halide addition to cobalt(II);[2e,f,i] halide abstraction by a Co(III) complex bearing redox-active ligands has also been reported[13]). The aryl halide could displace N_2 from $LCo(N_2)$ and then undergo C−X cleavage to release the free aryl radical, which would independently find its way to a second $LCo(N_2)$ molecule. Stabilized radicals are less likely to undergo side reactions, explaining the improved LCoAr yields for entries 7−9 and 20. The faster reactions of bromides and iodides would result in higher radical concentrations and hence formation of more biaryl side products. The alternative sequence of initial mononuclear oxidative addition followed by aryl transfer to unreacted $LCo(N_2)$ seems unlikely;[14] in particular, the required side-on C−Br coordination of BrC_6H_2-2,4,6-$^tBu_3$ to the LCo fragment is impossible for steric reasons.

Alkyl halides RX (X = Cl, Br, I) also react, and selectivities show similar trends: faster reactions, but less LCoR formation, for activated halides (benzyl) and for bromides vs chlorides. Methyl iodide, however, produced an unexpectedly high yield of LCoMe (entry 15). Unactivated C−F bonds are not attacked (*n*-$C_8H_{17}F$, entry 22), but the allylic fluoride *n*-$C_6F_{13}CH$=CH_2 produced a reasonable amount of an alkyl complex tentatively identified as $LCo(\sigma\text{-}CH_2CH{=}CFC_5F_{11})$.

DFT studies[15] support the proposed reaction sequence. Replacement of N_2 from $LCo(N_2)$ by terminally Cl-bound ClC_6H_5 is endergonic by about 10 kcal/mol (Figure 2). From this complex, the transition state for C−Cl bond cleavage is another 10 kcal/mol further uphill and shows the correct imaginary mode; this would constitute the rate-determining step. Further optimization results in full dissociation of an

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[11] Knijnenburg, Q.; Hetterscheid, D. G. H.; Kooistra, T. M.; Budzelaar, P. H. M. *Eur. J. Inorg. Chem.* **2004**, 1204.

[12] This difference may be related to the fact that the $^\bullet C_6H_2$-2,4,6-$^tBu_3$ radical has a fairly long lifetime, whereas $^\bullet C_6H_2$-2,4,6-Me_3 rearranges or reacts quickly: (a) Brunton, G.; Griller, D.; Barclay, L. R. C.; Ingold, K. U. *J. Am. Chem. Soc.* **1976**, *98*, 6803. (b) Childress, B. C.; Rice, A. C.; Shevlin, P. B. *J. Org. Chem.* **1974**, *39*, 3056.

[13] (a) Smith, A. L.; Clapp, L. A.; Hardcastle, K. I.; Soper, J. D. *Polyhedron* **2010**, *29*, 164. (b) Note that diiminepyridine ligands, like the iminobenzosemiquinonate ligands used by Soper, are redox-active,[5] so that in both their work and ours one could consider the actual reductant to be the ligand rather than the metal.

[14] We cannot exclude that the actual mechanism of oxidative addition is substrate-dependent (see e.g.: Affo, W.; Ohmiya, H.; Fujioka, T.; Ikeda, Y.; Nakamura, T.; Yorimitsu, H.; Oshima, K.; Imamura, Y.; Mizuta, T.; Miyoshi, K. *J. Am. Chem. Soc.* **2006**, *128*, 8068), varying from chlorine radical abstraction for unactivated halides to three-center oxidative addition followed by aryl radical loss for the more reactive halides. Neither our experimental work nor preliminary DFT calculations provide any indication of this; so for simplicity we assume a single common mechanism in the present work.

[15] Turbomole, b3-lyp functional, optimization and vibrational analysis using TZVP, final energies using TZVPP; for details see SI.

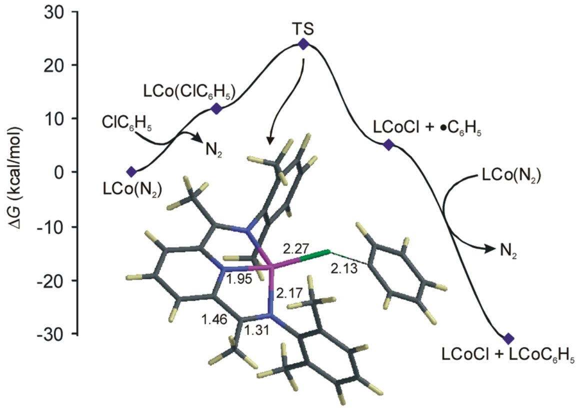

Figure 2. Calculated free energy profile (b3-lyp/TZVPP//b3-lyp/TZVP) for the binuclear oxidative addition of ClC_6H_5 at two $Co^{(0)}$ centers according to Scheme 1. Bond lengths (for the TS) are in Å.

aryl radical, which then combines with another LCo fragment to form the rather stable LCoAr. The calculated overall free energy barrier for this process (23.2 kcal/mol) is compatible with a process that is slow (hours) at room temperature.

In conclusion, this work demonstrates the first example of net binuclear oxidative addition of *aryl chlorides*. The characteristics of the reaction strongly suggest a radical mechanism, which is supported by calculations. Further efforts will be aimed at achieving C−C coupling of the resulting cobalt aryls in stoichiometric and catalytic reactions.[16,17]

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Supporting Information Available: Experimental and computational details, X-ray structure determination, coordinates and energies for calculated structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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(16) For an example of C−C bond formation involving radical chemistry at well-defined Ni centers, see: Jones, G. D.; Martin, J. L.; McFarland, C.; Allen, O. R.; Hall, R. E.; Haley, A. D.; Brandon, R. J.; Konovalova, T.; Desrochers, P. J.; Pulay, P.; Vicic, D. A. *J. Am. Chem. Soc.* **2006**, *128*, 13175, and references therein.

(17) There are numerous reports of C−C bond formation at cobalt involving incompletely characterized organocobalt intermediates; see for example ref 14 and (a) Cahiez, G.; Moyeux, A. *Chem. Rev.* **2010**, *110*, 1435. (b) Yorimitsu, H.; Oshima, K. *Pure Appl. Chem.* **2006**, *78*, 441; many of these reactions most likely involved radical chemistry.