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N-Assisted Carbon−Hydrogen Bond Activation by Cobalt(I) Complexes

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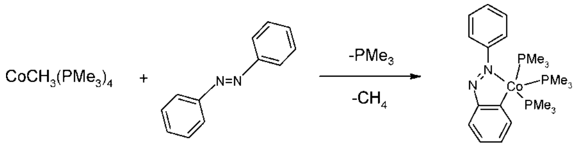
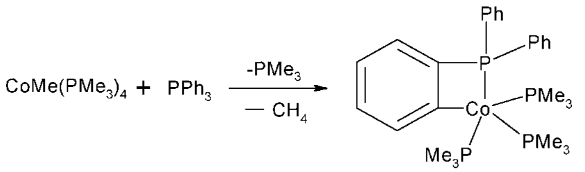
*Summary: Reactions of 2-(4′-R-phenylazo)-4-methylphenols (R = Me (**1**), Br (**2**)) with $Co(PMe_3)_3Cl$ afford two organocobalt(III) complexes, $Co(PMe_3)_2Cl(Me(C_6H_3O{\cap}N{=}NC_6H_3R)\cdot(H_2NC_6H_4R))$ (R = Me (**3**), Br (**4**)), whereas the reactions of **1** and **2** with $Co(PMe_3)_4$ and $Co(PMe_3)_4Me$ afford the dinuclear complex $[Co_2(PMe_3)_4(MeC_6H_3O{\cap}NH)_2]$ (**7**) with the cleavage of the N=N bond. Crystal structures of **3**, **4**, and **7** were determined by X-ray crystallography.*

There has been considerable current interest in the utilization of transition metals in promoting interesting chemical transformations of organic substrates. Such reactions often proceed via a C−H activation of the organic substrate, leading to the formation of a reactive organometallic intermediate, which then undergoes further reactions to yield the final product. Thus, C−H activation of hydrocarbons,[1] particularly that involving aromatic compounds and cyclometalation,[2] is an important area of research with respect to homogeneous catalysis. Klein reported C−H activation of ortho metalations of azobenzene[3] and phenyl phosphites[4] using cobalt complexes supported by trimethylphosphine (eqs 1 and 2).



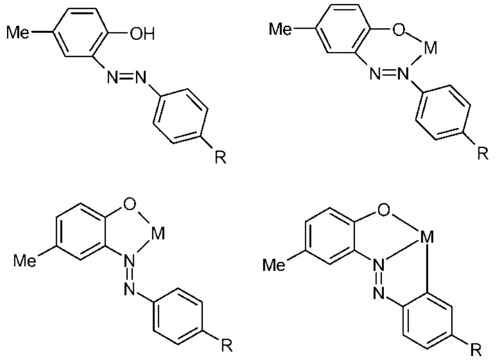
(1)



(2)

Transition-metal complexes that contain an azo ligand or its derivatives are well-known. Several coordination modes have been documented. However, 2-(arylazo)phenols usually bind to metal ions as bidentate [N,O]-donors, forming a five- or six-membered chelate ring.[5] In some cases, C−H activation from an ortho position of the pendant phenyl ring was observed. The 2-(arylazo)phenol derivative ligand serves as a [C,N,O]-donor by Ru,[6] Ir,[7] and Os[8] (Scheme 1).

Scheme 1



Herein we report on progress in the direction of cyclometalation reactions involving C−H bond activation at cobalt centers with 2-(arylazo)phenol as prechelate ligand in the reaction of 2-(arylazo)phenol with $Co(PMe_3)_3Cl$. The new ortho-chelated cobalt complexes were isolated and characterized. N=N cleavage reactions were also observed, and a dinuclear cobalt complex was obtained in the reactions of 2-(arylazo)phenol with $Co(PMe_3)_4$ and $Co(PMe_3)_4Me$. The related formation mechanisms of the complexes are discussed.

Reaction of $Co(PMe_3)_3Cl$ with 2-(Arylazo)phenols. Reactions of $Co(PMe_3)_3Cl$ with 2-(4′-R-phenylazo)-4-methylphenols (R = Me (**1**), Br (**2**)) afford the complex type $Co(PMe_3)_2Cl(Me(C_6H_3O{\cap}N{=}NC_6H_3R)\cdot(H_2NC_6H_4R)$ (R = Me (**3**), Br (**4**)) via C−H activation (eq 3).

Crystallization at 0 °C in diethyl ether afforded dark green crystals in 25% (**3**) and 29% yields (**4**) based on $Co(PMe_3)_3Cl$. The two compounds are stable at room temperature in the solid state for more than 4 h but quickly decompose in solution when exposed to air.

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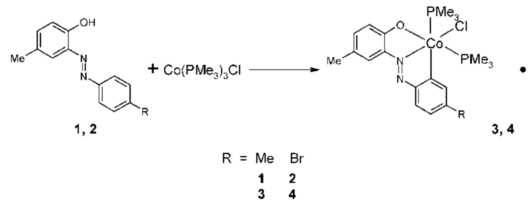

(3)

In the ^{1}H NMR spectra, the two trimethylphosphine ligands show a signal at 0.96 ppm for **3**. In the ^{31}P NMR spectra, signals of the PMe_3 ligands are registered at 7.74 ppm for **3**.

Complexes **3** and **4** have similar molecular structures (Figures 1 and 2).[9] They are composed of two components: the organocobalt complex and the organic part. The cobalt atom is hexacoordinate in an octahedral geometry, and the two trimethylphosphines are trans in axial positions with the angle P1−Co−P2 (170.35(12)°) in complex **3** and 173.32(6)° in complex **4**. The N═N lengths of 1.285(11) Å in complex **3** and 1.286(5) Å in complex **4** are in the range of normal N═N double bonds (1.22−1.30 Å).[6−8] The Co1−C1 bond (1.936(9) Å) in complex **3** is longer than the Co1−C25 bond (1.896(5) Å) in complex **4** because of the difference in electron properties between the methyl group (electron-donating group) in complex **3** and the bromo atom (electron-withdrawing group) in complex **4**. The organic part is 4-methylaniline in complex **3** and 4-bromoaniline in complex **4**, indicating the cleavage of the N═N bond.

The proposed formation mechanism of complexes **3** and **4** is suggested in Scheme 2. The first step is the coordination of the nitrogen atom of the azo function to the cobalt atom to give rise to the intermediate **5**. The C−H bond activation is supported and compensated through cyclometalation with the azo nitrogen as an anchoring group to form the hydrido intermediate **6**. This hydridocobalt species reacts with compound **1** or **2** with the participation of the phenoxy hydroxy group to afford complex **3** or complex **4** together with 4-methylaniline (or 4-bromoaniline), by hydrogen transfer to compound **1** (or **2**), through the cleavage of the azo function (reduction). Unfortunately, another byproduct, 2-amino-4-methylphenol, could not be experimentally verified. In earlier work the similar process with the reduction of 3-*tert*-butyl-5-methylsalicylaldehyde to 2-*tert*-butyl-6-(hydroxymethyl)-4-methylphenol by hydrogen transfer from the hydrido and phenoxy hydroxyl groups was also observed.[10] Instead of the product with two six-membered rings in that system, two five-membered chelate rings play an important role in this reaction for the formation of complexes **3** and **4**. The tridentate phenyl−azo−phenoxy [C,N,O]-ligand acts as a pincer ligand. Bruce thinks in some cases it would appear that formation of H_2 in the metalation is a more relatively difficult process than the small-molecule HCl elimination.[11] The metalation of the ligand by loss of hydrogen was reported with a hydridoiridium complex.[12] We think in our case the reduction with hydrogen occurs because of the presence of an active azo compound.

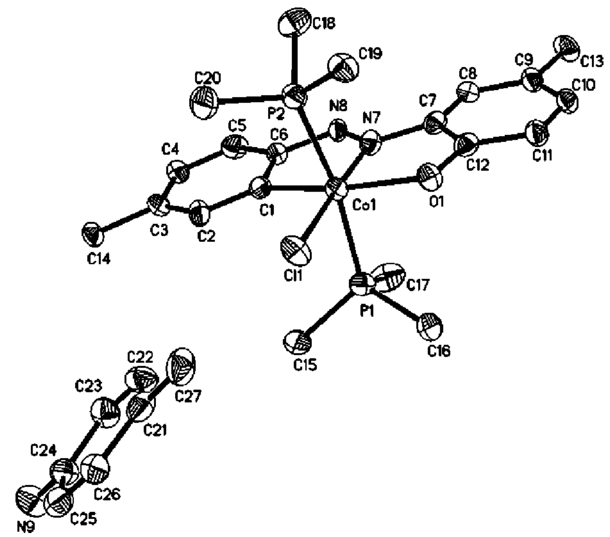

Figure 1. Molecular structure of **3** (all hydrogen atoms are omitted for clarity). Selected bond distances (Å) and angles (deg): Co1−N7 = 1.843(7), Co1−C1 = 1.936(9), Co1−O1 = 1.988(7), Co1−P1 = 2.210(3), Co1−P2 = 2.225(3), Co1−Cl1 = 2.279(3), N7−N8 = 1.285(11); N7−Co1−C1 = 81.9(4), N7−Co1−O1 = 83.7(3), C1−Co1−O1 = 165.5(3), N7−Co1−P1 = 94.2(2), C1−Co1−P1 = 88.8(2), O1−Co1−P1 = 92.2(2), N7−Co1−P2 = 94.2(2), C1−Co1−P2 = 87.7(3), O1−Co1−P2 = 93.47(19), P1−Co1−P2 = 170.35(12), N7−Co1−Cl1 = 177.2(3), C1−Co1−C11 = 101.0(2), O1−Co1−C11 = 93.47(19), P1−Co1−C11 = 85.97(12), P2−Co1−C11 = 85.89(9), N7−N8−C6 = 108.7(8).

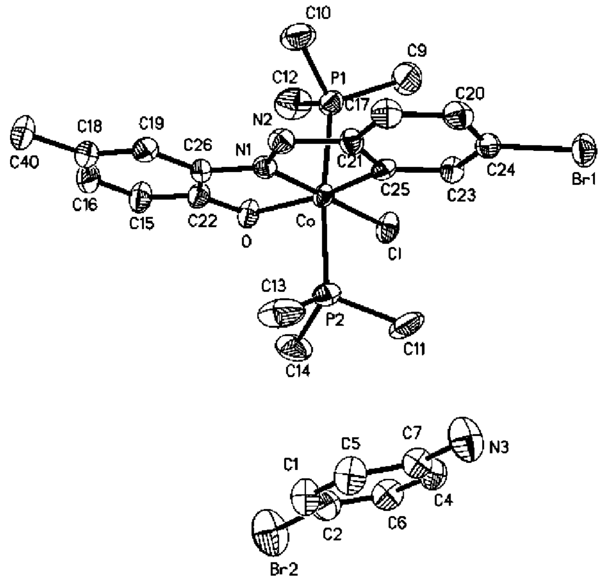

Figure 2. Molecular structure of **4** (all hydrogen atoms are omitted for clarity). Selected bond distances (Å) and angles (deg): Co−O = 2.014(3), Co−Cl = 2.2602(15), Co−N1 = 1.847(4), Co−C25 = 1.896(5), Co−P1 = 2.2359(17), Co−P2 = 2.2388(17), N1−N2 = 1.286(5); N1−Co−C25 = 82.2(2), N1−Co−O = 83.72(16), C25−Co−O = 165.86(19), N1−Co−P1 = 92.10(13), C25−Co−P1 = 88.43(15), P1−Co−O = 91.52(12), N1−Co−P2 = 93.86(13), C25−Co−P2 = 89.39(15), P2−Co−O = 92.14(12), P1−Co−P2 = 173.32(6), N1−Co−Cl = 178.28(13), C25−Co−Cl = 99.44(16), O−Co−Cl = 94.68(11), P1−Co−Cl = 87.30(6), P2−Co−Cl = 86.84(6), N1−N2−C21 = 108.7(4).

Reaction of $Co(PMe_3)_4$ and $Co(PMe_3)_4Me$ with 2-(Arylazo)phenols. Reactions of $Co(PMe_3)_4$ and $Co(PMe_3)_4Me$ with 2-(4′-R-phenylazo)-4-methylphenols (R = Me (**1**), Br (**2**)) afforded a kind of dinuclear cobalt(II) complex, $[Co(PMe_3)_2(MeC_6H_3O{\cap}NH)]_2$ (**7**). Complex **7** was isolated and characterized by X-ray diffraction. The *o*-phenoxy−imido−phenyl

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(9) CCDC-686118 (**3**), CCDC-686120 (**4**), and CCDC-686117 (**7**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB21EZ, U.K. (fax (+44)1223-336-033; email deposit@ccdc.cam.ac.uk).

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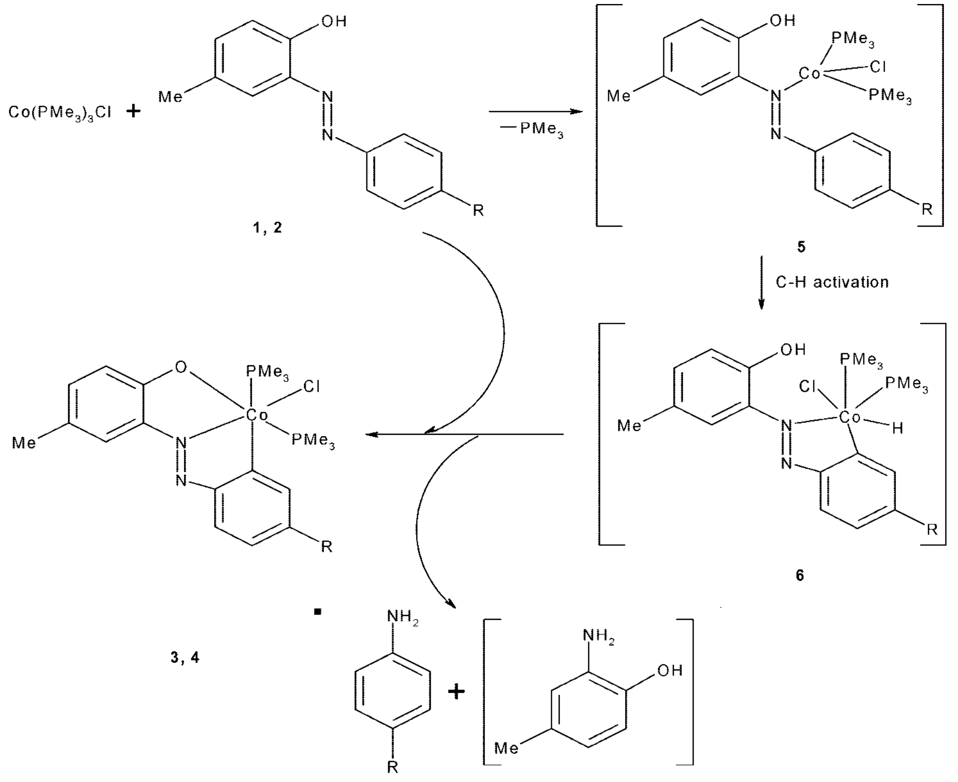
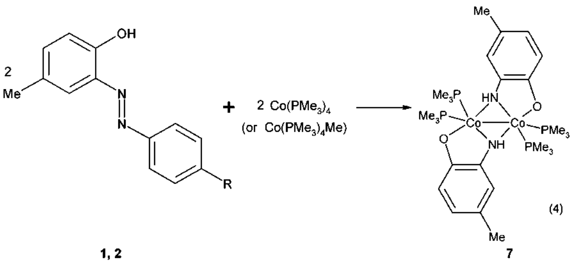
Scheme 2. Formation of Compounds 3 and 4



is a bridged ligand, formed through the cleavage of the N═N bond (eq 4). The reaction mechanism according to eq 4 is not clear, and more investigation on it is ongoing.



Crystallization at 0 °C afforded dark crystals of **7** in pentane and diethyl ether solution in 34−37% yield. The compound is very stable both in the solid state and in solution in the presence of moisture. The N−H stretching bands were recorded at 3283 and 3181 cm^{-1}, which are comparable with those of a bridging amide group.[13]

In the crystal structure of complex **7**[9] two imidophenolatobis(trimethylphosphine)cobalt(II) units are combined through an ordinary metal−metal bond (Co−Co = 2.3997(5) Å) which is almost symmetrically bridged by two NH groups (Co1−N−Co2 = 76.23(8) and 76.42(8)°) to give a butterfly-shaped [N2Co2] core (N−Co−N = 79.94(9)°) without a center of symmetry. The four trimethylphosphine ligands are pairwise attached to the cobalt atoms. Those ligands align with a [Co, N] vector. The axial Co−P bonds (Co1−P1 = 2.2469(8) and Co2−P2 = 2.2405(8) Å) are longer than those (Co1−P3 = 2.2110(8) and Co2−P4 = 2.214(7) Å) positioned trans to N atoms because of the strong [Co,Co] interaction, whereas the Co−N bonds of the two five-membered chelate rings (Co1−N2 = 1.918(2) and Co2−N1 = 1.922(2) Å) are shorter than the other two Co−N bonds (Co1−N1 = 1.966(2) and Co2−N2 = 1.961(2) Å).

In conclusion, reactions of 2-(4′-R-phenylazo)-4-methylphenols (R = Me (**1**), Br (**2**)) with $\mathrm{Co(PMe_3)_3Cl}$ afford

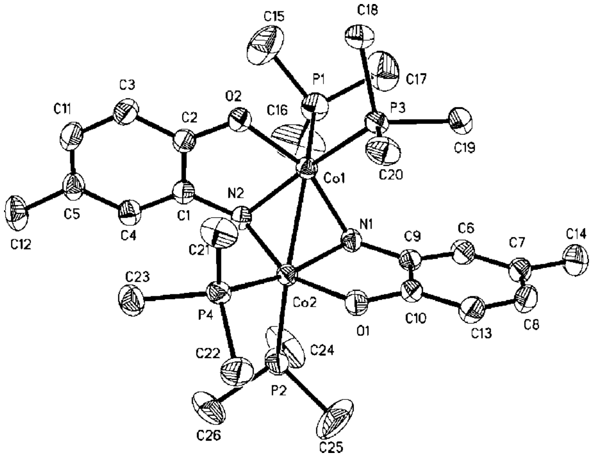


Figure 3. Molecular structure of **7** (all hydrogen atoms are omitted for clarity). Selected bond distances (Å) and angles (deg): Co1−N1 = 1.966(2), Co1−N2 = 1.918(2), Co1−O2 = 1.9706(18), Co1−P1 = 2.2469(8), Co1−P3 = 2.2110(8), Co1−Co2 = 2.3997(5), Co2−N1 = 1.922(2), Co2−N2 = 1.961(2), Co2−O1 = 1.9675(17), Co2−P2 = 2.2405(8), Co2−P4 = 2.214(7), O2−C2 = 1.325(3), O1−C10 = 1.319(3), N2−C1 = 1.412(3), N1−C9 = 1.419(3); N2−Co1−N1 = 79.94(9), N1−Co2−N2 = 79.95(9), N2−Co1−O2 = 84.41(8), P3−Co1−P1 = 99.02(3), N1−Co1−Co2 = 51.05(6), P3−Co1−Co2 = 112.77(2), P1−Co1−Co2 = 142.04(3), P4−Co2−P2 = 100.18(3), P4−Co2−Co1 = 112.98(2), P2−Co2−Co1 = 140.74(3), Co1−N1−Co2 = 76.23(8), Co1−N2−Co2 = 76.42(8), Co1−N2−C1 = 111.67(17), Co1−O2−C2 = 110.67(16), O2−C2−C1 = 118.9(2), C2−C1−N2 = 113.4(2).

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two organocobalt(III) complexes, $Co(PMe_3)_2Cl(Me(C_6H_3O{\cap}N{=}NC_6H_3R)\cdot(H_2NC_6H_4R)$ (R = Me (**3**), Br (**4**)), whereas the reactions of compounds **1** and **2** with $Co(PMe_3)_4$ and $Co(PMe_3)_4Me$ afford the dinuclear cobalt complex $[Co_2(PMe_3)_4(MeC_6H_3O{\cap}NH)_2]$ (**7**) with the complete cleavage of the N=N bond. Crystal structures of the complexes **3**, **4**, and **7** were determined by X-ray crystallography.

Acknowledgment. We gratefully acknowledge support by the NSF of China, Nos. 20772072 and 20872080.

Supporting Information Available: Text and tables giving experimental details and X-ray data for **3**, **4**, and **7** and CIF files giving X-ray data for **3**, **4**, and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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