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[7] New compounds have been fully characterized by spectroscopic methods and elemental composition (see Supporting Information).

[8] Crystal structure analysis of **2b**$\cdot$4CHCl$_3$: $C_{66}H_{58}Br_3Cl_{12}N_4P_3$, $M_r = 1665.20\,g\,mol^{-1}$, triclinic space group $P\bar{1}$, $a = 12.8432(4)$, $b = 14.7484(6)$, $c = 19.5242(5)$ Å, $\alpha = 85.839(2)$, $\beta = 89.058(2)$, $\gamma = 72.373(2)°$, $V = 3515.2(2)$ Å^3, $Z = 2$, unique data 15993 ($2\theta \leq 55°$), parameters 795, R_1 $[F^2 > 2\sigma(F^2)]$ 0.044, wR_2 (all data) 0.094. Crystal structure analysis of **4b**: $C_{67.5}H_{59}Cl_{15.26}N_4P_3$, $M_r = 779.85\,g\,mol^{-1}$, triclinic space group $P\bar{1}$, $a = 12.453(3)$, $b = 14.853(3)$, $c = 19.456(6)$ Å, $\alpha = 85.522(14)$, $\beta = 89.845(15)$, $\gamma = 72.399(12)°$, $V = 3419.0(15)$ Å^3, $Z = 2$, unique data 10508 ($2\theta \leq 48°$), parameters 796, R_1 $[F^2 > 2\sigma(F^2)]$ 0.190, wR_2 (all data) 0.422. The poor overall precision resulted from the presence of a great deal of disordered chloroform, coupled with poor overall crystal quality as a result of decomposition. The structural details of the macrobicycle are clear and unambiguous, however. CCDC-143862 (**2b**), and -172792 (**4b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit @ccdc.cam.ac.uk).

[9] The conventional assignment of the stereochemical descriptor *P* or *M* (helical twist sense) to the propeller units of the chiral macrobicycles was made by looking at the molecule along its threefold axis from the side of the tribenzylamine fragment.

[10] The activation energy was calculated from the equation: $\Delta G^{\neq} = (4.57 \times 10^{-3})\ T_c\ (10.32 + \log(T_c 2/\pi\Delta\nu))$ following: D. H. Williams, I. Fleming, *Spectroscopic Methods in Organic Chemistry*, 4th ed., McGraw-Hill, New York, **1989**, p. 103.

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[17] Semi-empirical calculations were carried out by using the MNDO method as implemented in the Gaussian 98 set of programs. The geometries of both stationary points were optimized, and harmonic frequency calculations were performed in order to characterize both structures as minima.

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Alkene C−H Activations at Dinuclear Complexes Promoted by Oxidation**

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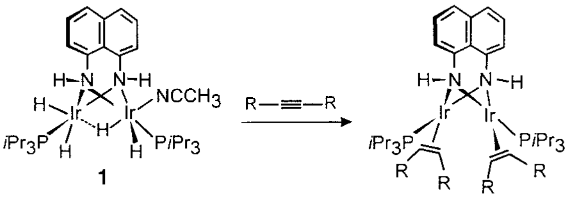
Several recent discoveries in the chemistry of transition metal di- and polynuclear complexes have disclosed new methods of hydrocarbon activation and functionalization, favored by polynuclear environments.[1, 2] In parallel, considerable progress has been made in understanding the reactivity features resulting from multimetallic reaction sites.[1, 3, 4] Together, such advances may contribute to the rational design of new catalysts and applications based on this type of compound. However, the proximity of the metal centers is likely to have significant repercussions for the reactivity, which remain to be determined.

In our recent studies on "open-book" d^8 diiridium complexes with N-donor bridges, we have observed a remarkable substrate selectivity in the reactions of these compounds towards oxidative addition reactants. Whereas the d^8 diiridium complexes underwent fast S$_N$2 oxidative additions with substrates such as halocarbons,[4] the additions of less-polar reactants such as dihydrogen were not observed. The oxidation of these d^{8}d^8 diiridium compounds, to species of d^{6}d^8 or d^{7}d^7 electronic configurations, gave dihydrogen-activating compounds.[5] Here we report that such an oxidation strategy also allows the transformation of nonreactive d^{8}d^8 compounds into dinuclear C−H activating species.

The treatment of the diamidonaphthalene ((NH$_2$)naphth)-bridged diiridium(III) complex [Ir$_2$(μ-1,8-(NH)$_2$naphth)(μ-H)H$_3$(NCCH$_3$)(P*i*Pr$_3$)$_2$] (**1**) with two equivalents of an internal alkyne such as 2-butyne or diphenylacetylene afforded diiridium(I) derivatives of the formula [Ir$_2$(μ-1,8-(NH)$_2$naphth)(η^2-*Z*-RHC=CHR)$_2$(P*i*Pr$_3$)$_2$] (R = Me (**2**), Ph (**3**)) [Eq. (1)]. The solution NMR spectra of both compounds indicate symmetric C_2 structures with a transoid arrangement of nonrotating *Z*-alkene ligands. These features have been confirmed by the X-ray crystallographic determination of the structure of **2**,[6] (Figure 1).



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R = CH$_3$, **2**
R = Ph, **3**

(1)

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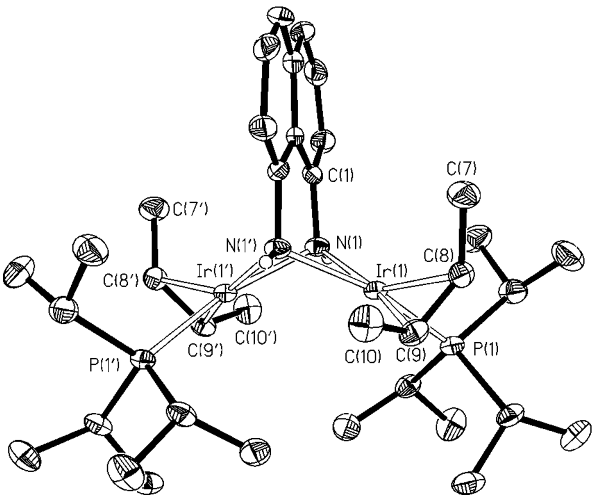


Figure 1. Molecular representation of the dinuclear complex **2**. Atoms labeled with a prime are related to the corresponding unprimed ones by the symmetry transformation $1-x, y, -z+3/2$. Selected interatomic distances [Å] and angles [°]: Ir(1)···Ir(1′) 2.9863(3), Ir(1)-P(1) 2.2336(10), Ir(1)-N(1) 2.124(3), Ir(1)-N(1′) 2.125(3), Ir(1)-C(8) 2.111(4), Ir(1)-C(9) 2.158(4), C(8)-C(9) 1.414(6); P(1)-Ir(1)-N(1) 97.32(10), P(1)-Ir(1)-N(1′) 164.34(9), N(1)-Ir(1)-N(1′) 72.62(16), N(1′)-Ir(1)-C(9) 91.28(15), C(7)-C(8)-C(9) 123.3(4), C(8)-C(9)-C(10) 121.5(4).

The alkene ligands of compounds **2** and **3** were found to be relatively nonlabile, they remained coordinated after the treatment of **2** and **3** with an excess of ligands such as pyridine, ethylene, or alkynes, but were slowly replaced by CO to give the known complex $[Ir_2(\mu\text{-}1,8\text{-}(NH)_2naphth)(CO)_2(PiPr_3)_2]$.[5] The oxidation of **2** and **3** by $[FeCp_2](CF_3SO_3)$ took place under conditions similar to those employed for the oxidation of related diiridium(I) derivatives to metal–metal bonded diiridium(II) species.[5] Instead of the expected diiridium(II) oxidation products, the reactions afforded the hydride-bridged diiridium(III) complexes **4** and **5** [Eq. (2)], after the oxidative addition of an alkene ligand C–H bond.

As indicated by the structures deduced for **4** and **5**, the selectivity of the C–H activation step is dependent on the nature of the alkene ligand. Whereas the *Z*-stilbene ligand of **3** was activated to give an alkenyl group, the *Z*-2-butene moiety of complex **2** underwent an allylic activation to afford a more stable η^3-allyl ligand.[7] The reaction sequence which leads to **4** and **5** also influences the nonactivated alkene ligands, which were labilized and substituted by acetonitrile solvent molecules.

Figure 2 shows the X-ray structure of complex **4**,[8] in which the bridging hydride atom is nonequidistant from the metal atoms. Such an asymmetric position, which is most likely the result of the different *trans* influences exerted by the ligands *trans* to this bridge,[3c, 9] is also inferred from the solution ^1H NMR signal of the hydride atom: a doublet of doublets at $\delta = -20.14$ with $J(H,P)$ coupling constants of 7.8 and 3.3 Hz. A similar pattern is found for the bridging-hydride ^1H NMR signal of the starting complex **1**, which also suggests an asymmetric position for this bridge. The hydride ligand of **5** displays a ^1H NMR signal in CD_2Cl_2, which consists of a doublet of doublets at $\delta = -17.86$ with $J(H,P)$ coupling constants of 49.5 and 11.1 Hz. The large value of the former coupling constant indicates a bridging hydride *trans* to one $PiPr_3$ ligand,[5] which supports the proposed structure depicted in Equation (2). This proposal is also consistent with the presence in the ^1H NMR spectrum of a singlet at $\delta = 6.86$, which corresponds to the vinylic hydrogen, and three singlets at $\delta = 1.03$, 2.55, and 2.90, attributed to three nonequivalent acetonitrile ligands.

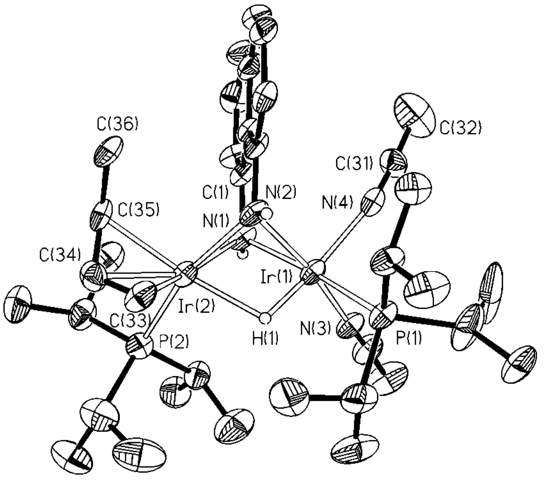
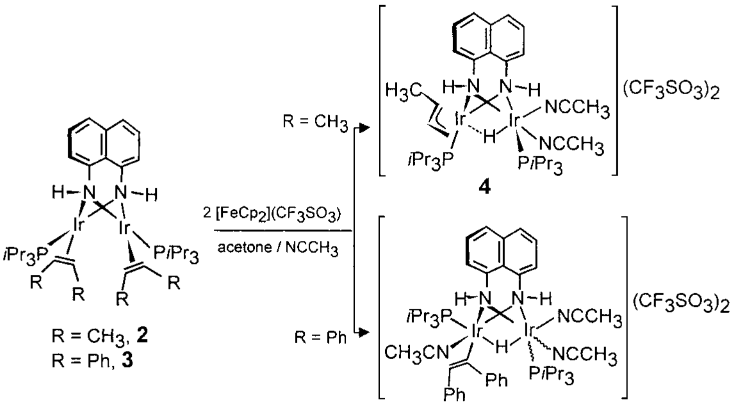


Figure 2. Molecular representation of the dicationic complex **4**. Selected interatomic distances [Å] and angles [°]: Ir(1)···Ir(2) 2.6938(4), Ir(1)-P(1) 2.3297(19), Ir(1)-N(1) 2.136(6), Ir(1)-N(2) 2.066(6), Ir(1)-N(3) 2.020(6), Ir(1)-N(4) 2.064(7), Ir(1)-H(1) 1.48(7), Ir(2)-H(1) 1.93(7), Ir(2)-P(2) 2.327(2), Ir(2)-N(1) 2.090(7), Ir(2)-N(2) 2.130(6), Ir(2)-C(33) 2.170(8), Ir(2)-C(34) 2.122(9), Ir(2)-C(35) 2.157(7), C(33)-C(34) 1.380(13), C(34)-C(35) 1.421(12); P(1)-Ir(1)-N(1) 170.82(19), N(2)-Ir(1)-N(3) 167.0(2), N(4)-Ir(1)-H(1) 174(3), P(2)-Ir(2)-N(2) 163.23(16), N(1)-Ir(2)-C(33) 161.1(3), C(35)-Ir(2)-H(1) 158(2), C(33)-C(34)-C(35) 119.6(9), C(34)-C(35)-C(36) 122.3(9).



R = CH$_3$, **2**
R = Ph, **3**

4

5

(2)

The reactivity described above indicates that the C–H oxidative addition capability of these d^8 dinuclear complexes is enhanced upon oxidation. This behavior, which apparently contradicts well-established ideas about oxidative addition to metal complexes, can be rationalized if the molecular orbital features typical of these compounds are considered. It has been shown that the bending of these dinuclear molecules towards the open-book structure is caused by attractive metal ⋯ metal interactions, which result from donor–acceptor interactions between the full d_{z^2} and the empty p_z orbitals of the two d^8 metal atoms.[10] The involvement of the p_z orbitals in such weak interactions could reduce their availability for other purposes, such as the C–H bond pre-coordination required for an oxidative addition,[11] thus accounting for the inertness of these d^8 compounds towards C–H bonds. A likely consequence of the partial oxidation of the d^8d^8 core is the modification of such an unfavorable orbital situation to give more accessible empty orbitals and consequently an enhanced C–H activation capability.

The chemistry herein illustrates the profound effect that weak intermetallic interactions exert upon the reactivity of dinuclear compounds. The inertness induced by such weak interactions in open-book d^8 dinuclear compounds appears to cause the promotion of C–H oxidative additions by oxidation, a result hardly predictable from the chemistry of mononuclear complexes.

Experimental Section

All compounds gave correct elemental analyses. In the spectroscopic data lists, the signals corresponding to the P*i*Pr$_3$ and to the naphthalene protons and carbons have been omitted.

1: The compound was prepared as a white solid (62 % yield) following the procedure described in[9] for its bispyrazolate-bridged analogue. ^{1}H NMR (300 MHz, [D$_6$]benzene, 293 K): $\delta = -23.15$ (dd, J(H,P) = 21.3 Hz, J(H,H) = 8.7 Hz, 1 H, Ir-H), -22.18 (ddd, J(H,P) = 24.9, 2.1 Hz, J(H,H) = 8.7 Hz, 1 H, Ir-H), -20.36 (dd, J(H,P) = 20.4 Hz, J(H,H) = 3.6, 1 H, Ir-H), -19.93 (ddd, 1 H, J(H,P) = 12.9, 2.1 Hz, J(H,H) = 3.6 Hz, Ir-H-Ir), 0.20 (s, NCCH$_3$, 3 H), 4.22 (br, 2 H, NH); ^{31}P{^{1}H} NMR (121 MHz, [D$_6$]benzene, 293 K): $\delta = 29.72$ (s), 39.12 (s); ^{13}C{^{1}H} NMR (75 MHz, [D$_6$]benzene, 293 K): $\delta = -0.18$ (s, NC*C*H$_3$), 114.36 (s, N*C*CH$_3$); MS (FAB$^+$, benzene): *m*/*z* [%]: 864 (100) [$M^+ - $NCCH$_3$].

2 and **3**: A solution of **1** (200 mg, 0.22 mmol) in toluene (10 mL) was treated with the alkyne (0.45 mmol) and stirred for 8 h at 293 K (**2**) or at 323 K (**3**). The red solid, formed after the concentration of the solution to about 2 mL, was separated from the liquid by decantation, washed with methanol and dried in vacuo. **2**: Yield: 180 mg, 84 %; ^{1}H NMR (300 MHz, [D$_6$]benzene, 293 K): $\delta = 0.95$ (d, J(H,H) = 6.2 Hz, 6 H, CHC*H*$_3$), 1.09 (d, J(H,H) = 6.9 Hz, 6 H, CHC*H*$_3$), 2.06 (q, J(H,H) = 6.2 Hz, 2 H, C*H*CH$_3$), 3.16 (q, J(H,H) = 6.9 Hz, 2 H, C*H*CH$_3$), 5.28 (br, 2 H, NH); ^{31}P{^{1}H} NMR (121 MHz, [D$_6$]benzene, 293 K): $\delta = 13.83$ (s); ^{13}C{^{1}H} NMR (75 MHz, [D$_6$]benzene, 293 K): $\delta = 11.52$ (s, CH*C*H$_3$), 14.54 (s, CH*C*H$_3$), 23.73 (s, *C*HCH$_3$), 42.78 (s, *C*HCH$_3$). **3**: Yield: 226 mg, 82 %; ^{1}H NMR (300 MHz, [D$_6$]benzene, 293 K): $\delta = 3.33$ (d, J(H,H) = 9.3 Hz, 2 H, CHPh), 4.71 (dd, J(H,P) = 9.6 Hz, J(H,H) = 9.3 Hz, 2 H, CHPh), 5.10 (br, 2 H, NH), 6.62–7.08 (m, 20 H, CH); ^{31}P{^{1}H} NMR (121 MHz, [D$_6$]benzene, 293 K): $\delta = 9.96$ (s); ^{13}C{^{1}H} NMR (75 MHz, [D$_6$]benzene, 293 K): $\delta = 31.66$ (s, CHPh), 44.25 (s, CHPh), 123.08, 124.90, 126.70, 127.30, 129.45, 130.22 (all s, CH), 145.30, 140.41 (s, C).

4 and **5**: A solution of complex **2** or **3**, respectively, in acetone/acetonitrile (0.10 mmol, 5 mL) was treated with [FeCp$_2$](CF$_3$SO$_3$) (0.20 mmol). After the color of the solution changed from red to yellow, the solution was evaporated to dryness and the residue treated with diethyl ether. A yellow solid was obtained by separation from the liquid by decantation and washing with diethyl ether. **4**: Yield 104 mg, 78 %; ^{1}H NMR (300 MHz, [D$_6$]acetone, 293 K): $\delta = -20.14$ (dd, J(H,P) = 7.8, 3.3 Hz, 1 H, Ir-H-Ir), -0.42 (d, J(H,H) = 6.6 Hz, CH$_3$), 1.70 (s, 3 H, NCCH$_3$), 2.85 (s, 3 H, NCCH$_3$), 2.88 (m, 1 H, CH$_2$), 4.08 (dd, J(H,H) = 5.1, 1.5 Hz, 1 H, CH$_2$), 4.64 (m, 1 H, CH), 4.83 (dq, J(H,H) = 6.6, 6.3 Hz, 1 H, CH), 5.35 (br, 1 H, NH), 6.66 (br, 1 H, NH); ^{31}P{^{1}H} NMR (121 MHz, [D$_6$]acetone, 293 K): $\delta = 3.41$ (s), 11.78 (s); ^{13}C{^{1}H} NMR (75 MHz, [D$_6$]acetone, 293 K): $\delta = 1.48$ (s, NC*C*H$_3$), 4.21 (s, NC*C*H$_3$), 14.14 (s, CH$_3$), 40.66 (s, CH), 42.31 (s, CH$_2$), 81.15 (s, CH), 121.79 (s, N*C*CH$_3$), 122.06 (s, N*C*CH$_3$), 122.41 (q, J(C,F) = 322.4 Hz, CF$_3$SO$_3$). **5**: Yield 96 mg, 64 %; ^{1}H NMR (300 MHz, CD$_2$Cl$_2$, 293 K): $\delta = -17.86$ (dd, J(H,P) = 49.5, 11.1 Hz, 1 H, Ir-H-Ir), 1.03 (s, 3 H, NCCH$_3$), 2.55 (s, 3 H, NCCH$_3$), 2.90 (s, 3 H, NCCH$_3$), 5.76 (br, 1 H, NH), 6.15 (br, 1 H, NH), 6.70 (d, J(H,H) = 7.2 Hz, 2 H, CH), 6.86 (s, 1 H, -CH), 6.91 (t, J(H,H) = 7.2 Hz, 1 H, CH), 6.95 (d, J(H,H) = 7.5 Hz, 2 H, CH), 7.00 (t, J(H,H) = 7.2 Hz, 2 H, CH), 7.05 (t, J(H,H) = 7.2 Hz, 1 H, CH), 7.15 (dd, J(H,H) = 7.5, 7.2 Hz, 2 H, CH). ^{31}P{^{1}H} NMR (121 MHz, [D$_6$]acetone, 293 K): $\delta = 14.15$ (s), 17.15 (s); ^{13}C{^{1}H} NMR (75 MHz, CD$_2$Cl$_2$, 293 K): $\delta = 1.58$ (s, NC*C*H$_3$), 4.75 (s, NC*C*H$_3$), 5.20 (s, NC*C*H$_3$), 117.53 (s, N*C*CH$_3$), 121.34 (s, N*C*CH$_3$), 123.52 (s, N*C*CH$_3$), 125.49, 125.63, 127.92, 128.25, 128.78, 129.11 (all s, CH), 133.40 (d, J(C,P) = 7.1 Hz, Ir-C), 141.09 (s, C), 141.92 (s, =CH), 148.84 (s, C).

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[6] A crystallographic imposed two-fold symmetry was observed relating the two halves of the dinuclear complex. Crystal data for **2**: $C_{36}H_{66}Ir_2N_2P_2$, $M_r = 973.24$, truncated octahedron ($0.21 \times 0.24 \times 0.28$ mm), orthorhombic, space group *Pbcn*, $a = 17.0149(13)$, $b = 15.7320(12)$, $c = 14.0527(11)$ Å, $V = 3761.6(5)$ Å^{-3}, $Z = 4$, $\rho_{calcd} = 1.719$ g cm^{-3}, $F(000) = 1920$, $T = 173(2)$ K, Mo$_{K\alpha}$ radiation ($\lambda = 0.71073$ Å, $\mu = 7.179$ mm^{-1}). Bruker SMART APEX CCD diffractometer. 22 837 measured reflections (2θ: 3.5–57.2°, ω scans 0.3°), 4570 unique ($R_{int} = 0.0576$); multiscan absorption correction applied (SADABS program), with min./max. transm. factors 0.176/0.254. Structure solved by Patterson and difference-Fourier maps; refined using SHELXTL. Final agreement factors were $R1 = 0.0283$ (3608 observed reflections, $F^2 > 4\sigma(F^2)$) and $wR2 = 0.0543$; data/restrains/parameters 4570/0/215; GoF = 0.972. Largest peak and hole 0.98 and -1.53 e Å^{-3}. CCDC-169454 (**2**) and -169455 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit @ccdc.cam.ac.uk).

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[8] Crystal data for **4** $0.5\,C_4H_{10}O$: $C_{38}H_{64}F_6Ir_2N_4O_6P_2S_2 \cdot 0.5\,C_4H_{10}O$, $M_r = 1334.45$, monoclinic, $P2_1/n$, $a = 12.1052(9)$, $b = 22.6941(17)$, $c = 20.0793(15)$ Å, $\beta = 97.820(1)°$, $V = 5464.8(7)$ Å^{-3}, $Z = 4$, $\rho_{calcd} =$

$1.622\,\mathrm{g\,cm^{-3}}$, $F(000) = 2636$, $\mu = 5.064\,\mathrm{mm^{-1}}$. Data collected as described for **2** with an irregular block ($0.35 \times 0.19 \times 0.08$ mm). 35819 measured reflections, 12913 unique; a multiscan absorption correction was performed (SADABS program), with min./max. transm. factors 0.421/0.727. Structure solution and refinement as described for **2**. Final agreement factors were $R1 = 0.0520$ (8227 observed reflections) and $wR2 = 0.1088$. Data/restrains/parameters 12913/7/631; GoF = 0.949. Largest peak and 2.358 and $-1.238\,\mathrm{e\,Å^{-3}}$.

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Bis(1,2,3,4-η^4-anthracene)cobaltate(1 −)**

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Dedicated to Professor Klaus Jonas

Polycyclic aromatic hydrocarbon (PAH or polyarene)[1] anion mediated reductions of transition metal halides and related substances provide convenient and sometimes unique routes to a variety of polyarene metal complexes and derived species.[2] Since the polyarene ligands may be labile and easily displaced by a variety of small molecules, polyarene metal complexes are potential sources of highly unsaturated metallic units in chemical synthesis.[3] Homoleptic systems are of particular interest since these species may function as "naked" metal atom reagents and are therefore valuable precursors for the general exploration of low-valent transition metal chemistry.[4] Except for the first reported homoleptic polyarene transition metal complex $[\mathrm{Ru(C_{10}H_8)_2}]^{2+}$ ($\mathrm{C_{10}H_8}$ = naphthalene),[5] all previous examples contained only early (Groups 4–6) transition metals.[4] However, the existence of this cationic ruthenium species suggested that related neutral and anionic polyarene complexes of later transition metals should also be accessible. We now report on the first anion of this type and the initial homoleptic polyarene complex of cobalt, bis(η^4-anthracene)cobaltate(1 −) (**1**). The only previously known homoleptic anthracene transition metal complex is bis(anthracene)chromium(0), which was prepared by the reaction of chromium vapor and anthracene in a metal atom reactor.[4c]

Reduction of cobalt(II) bromide by three equivalents of potassium anthracene in tetrahydrofuran (THF) at −55 to −65 °C provided a dark red solution, from which deep red, nearly black, microcrystals of **1** as $[\mathrm{K([2.2.2]cryptand)}]^+$ or $[\mathrm{K([18]crown\text{-}6)(THF)_2}]^+$ salts were isolated in 82–87% yields (see Experimental Section for details; [Eq. (1)]). Corresponding reductions conducted with alkali metal naphthalenes provided much less thermally stable solutions of a presumably analogous bis(naphthalene)cobaltate(1 −).

$$\mathrm{CoBr_2} + 3\,\mathrm{KC_{14}H_{10}} \xrightarrow[-60\,^\circ\mathrm{C}]{\mathrm{THF}} \xrightarrow[-2\,\mathrm{KBr}]{\mathrm{L}} [\mathrm{KL(THF)}_x][\mathrm{Co(C_{14}H_{10})_2}]\cdot y\,\mathrm{THF} + \mathrm{C_{14}H_{10}} \tag{1}$$

1a: L = [2.2.2]cryptand, $x = 0$; $y = 1/2$; 82%
1b: L = [18]crown-6, $x = 2$; $y = 0$; 87%

Although this substance is highly reactive towards a number of substrates, for example, it readily reacts with carbon monoxide at normal pressures and −60 °C° to produce $[\mathrm{Co(CO)_4}]^-$, all attempts to isolate this interesting species have so far failed.[6] Interestingly, the reduction of cobaltocene by three equivalents of potassium naphthalene provided a similarly labile source of $\mathrm{Co^{I-}}$, which also defied isolation and characterization.[7]

^{1}H and ^{13}C NMR spectra of **1** were independent of the cation and established that its stoichiometry in solution is identical to that observed in the solid state (vide infra). ^{1}H, ^{13}C correlated NMR spectra of **1** exhibited two equally intense quaternary ^{13}C signals at $\delta = 134.1$ and 146.0, which are indicative of two equivalent η^4-anthracenes bound through one peripheral ring each to cobalt.[8] ^{1}H NMR spectra of **1** are also consistent with the presence of two identical anthracene groups bound in the same fashion to cobalt (see Experimental Section). These resonance positions and patterns are consistent with those previously observed for other η^4-anthracene transition metal complexes,[9] and provide compelling evidence for the presence of discrete bis(1,2,3,4-η^4-anthracene)cobaltate(1 −) units in solution.

Single-crystal X-ray studies on **1a** and **1b** were carried out[10] and confirmed the formulation of **1** based on NMR data and elemental analyses. The cations in these salts are unexceptional and well separated from anions in the crystalline lattices. Since the structures of **1** in both salts show nearly identical features, but the cobaltate in **1a** suffered from slight disorder in one anthracene ring, only **1b** will be described herein. The coordination environment about the cobalt is distorted tetrahedral, as defined by midpoints of the outer C–C bonds of the coordinated diene units (Figure 1), and resembles that previously observed in $[\mathrm{Co}(\eta^4\text{-1,4-di-}tert\text{-butylbuta-1,3-diene})_2]^-$ (**2**).[11] Analogous Co–C and C–C distances of the cobalt-diene units in **1b** and **2** are also very similar, suggesting that the Co–C interactions in both species are closely related. For example, the respective C–C distances of the coordinated diene units in **1b** and **2** show no significant variation.[12] This situation is typical of later transition metal conjugated diene complexes, such as the d^8 Fe^0 complex, η^4-butadiene iron tricarbonyl,[13] in which metal π donation (backbonding) is not so important as it is in related early

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