Electron transfer-induced replacement of carbonyl ligands in cobalt clusters

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Activation of carbonyl clusters through their oxidation for the replacement of carbonyl ligands is not documented. This is due to their high oxidation potential and the instability of the resulting radical cations.[1] In the present work, we proposed a new approach to the replacement of carbonyl ligands involving the oxidation of an electroactive organometallic group linked through a conducting chain to the cluster fragment rather than the cluster itself. Derivatives **1** in which the electroactive group[2] Cp*(dppe)Fe is linked by the acetylenide bridge with a Co_2C_2-type cluster were chosen as the starting compounds. These complexes were prepared by the standard procedure[3] (Scheme 1).

Scheme 1

$$Cp^*(dppe)FeC{\equiv}CC{\equiv}CR + Co_2(CO)_8 \longrightarrow$$

$$\longrightarrow Cp^*(dppe)FeC{\equiv}CC_2R[Co_2(CO)_6]$$

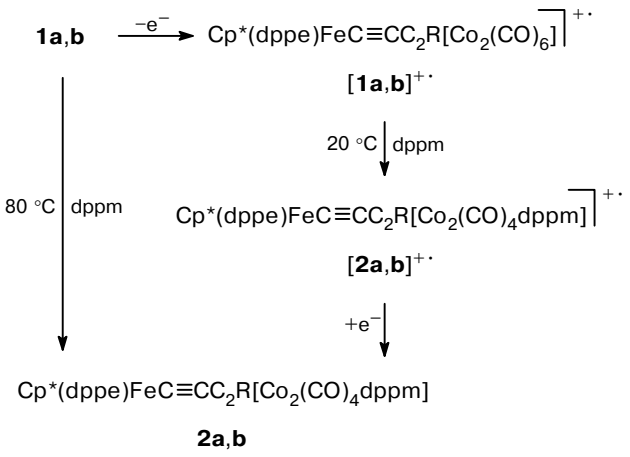
1a,**b**

R = H (**a**), $SiMe_3$ (**b**)

It was found that the oxidation of compound **1** with Cp_2FeBF_4 gives labile radical cations $[\mathbf{1a},\mathbf{b}]^{+\cdot}$ (IR, ν/cm^{-1}: 2096, 2062, 2038 (s, CO); ESR, $g = 2.26$). The addition of diphenylphosphinomethane (dppm) to radical cation $[\mathbf{1a},\mathbf{b}]^{+\cdot}$ causes replacement of two carbonyl ligands under mild conditions and gives rise to stable radical cations $[\mathbf{2a},\mathbf{b}]^{+\cdot}$ (Scheme 2), which can be isolated in the individual state. One-pot reduction of radical-cation complexes $[\mathbf{2a},\mathbf{b}]BF_4$ with Cp_2Co yielded neutral diamagnetic compounds **2a**,**b**. The total yield of the conversion **1a**,**b** → **2a**,**b** was ~70%.

Complexes **2a**,**b** were characterized by data from elemental analysis, IR spectroscopy, and ^1H and ^{31}P NMR spectroscopy. Although complexes **2a**,**b** can be obtained from compounds **1a**,**b** in one step, this conversion requires more drastic conditions and provides significantly lower yields because of the formation of decomposition products.

Scheme 2



Thus, the present work demonstrated the potentiality of this approach, which can serve as a model of molecular devices for a switch-on (oxidation)—switch-off (reduction) scheme.

All manipulations relating to the synthesis and isolation were carried out in an atmosphere of argon with the use of anhydrous solvents. IR spectra were recorded on a Magna 750 instrument (Nikolet) (resolution 2 cm^{-1}) in CH_2Cl_2. NMR spectra were recorded on a Bruker AMX-400 instrument (400.13 MHz) with (^1H) Me_4Si as the internal standard and (^{31}P) 85% H_3PO_4 as the external standard. ESR spectra were recorded on a Varian E-12 spectrometer equipped with a double resonator (for a test sample and a standard).

[(Pentamethylcyclopentadienyl)(bisdiphenylphosphinoethane)iron(II)]bis(diphenylphosphinomethane)tetracarbonyldicobalt](μ-η^1,η^2-butadiynyl) (2a) was obtained by oxidation of compound **1a** (0.0185 g, 0.02 mmol) with Cp_2FeBF_4 (0.0055 g, 0.02 mmol) in 5 mL of CH_2Cl_2 over 20 min followed by addition of dppm (0.0077 g, 0.02 mmol) and stirring at ~20 °C for 1.5 h. A solution of Cp_2Co (0.0038 g, 0.02 mmol) in 2 mL of CH_2Cl_2 was added to the reaction mixture, and stirring was continued for an additional hour. The solvent was removed *in vacuo*, and the products were extracted with hexane. The extract was filtered under argon through a layer of Celite and kept in a refrigerator. The black-

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green crystals that formed were dried in a water bath (50 °C) *in vacuo* to give compound **2a** (0.0182 g, 73%). Found (%): C, 67.00; H, 5.48. $C_{69}H_{62}O_4Co_2FeP_4$. Calculated (%): C, 66.15; H, 4.99. IR, ν/cm^{-1}: 2019, 1979, 1952 (s, CO). ^{1}H NMR (C_6D_6), δ: 1.69 (s, 15 H, Me); 2.10, 2.99 (both m, 2 H each, CH_2CH_2); 2.84, 3.26 (both m, 1 H each, CH_2); 5.79 (t, 1 H, CH, J_{HP} = 8.8 Hz); 7.0—8.2 (m, 40 H, Ph). ^{31}P NMR, δ: 42.03 (s); 99.82 (s).

[(Pentamethylcyclopentadienyl)(bisdiphenylphosphinoethane)iron(II)](bisdiphenylphosphinomethane)tetracarbonyldicobalt](μ-η^1,η^2-trimethylsilylbutadiynyl) (2b) was obtained analogously in 68% yield. IR, ν/cm^{-1}: 2012, 1977, 1949 (s, CO). ^{1}H NMR (C_6D_6), δ: 0.51 (s, 9 H, $SiMe_3$); 1.75 (s, 15 H, Me); 2.30, 3.22 (both m, 2 H each, CH_2CH_2); 2.80, 3.36 (both m, 1 H each, CH_2); 6.79—8.09 (m, 40 H, Ph). ^{31}P NMR, δ: 33.42 (s); 100.03 (s).

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References

1. B. H. Robinson and J. Simpson, in *Paramagnetic Organometallic Species in Activation/Selectivity Catalysis,* Ed. M. Chanon, Kluwer, Dordrecht, The Netherlands, 1989, 357 pp.
2. F. Paul and C. Lapinte, *Coord. Chem. Rev.*, 1999, **99**, 1863.
3. R. S. Dickson and D. F. Frazer, *Adv. Organomet. Chem.*, 1974, **12**, 323.

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