from triplet states of a ligand-to-metal charge transfer character that mix with metal-centered (ds/dp) states modified by Au ··· Au interactions (LMMCT; S → Au), whereas the high-energy emission at ca. 500 nm is attributed to metal-perturbed intraligand phosphorescence.

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[10] **1**: Elemental analysis calcd for $[Au_{10}(\mu\text{-PNP})_4(\mu_3\text{-S})_4](PF_6)_2 \cdot (CH_3)_2CO$ (found): C 32.08 (32.34), H 2.76 (2.75), N 1.38 (1.43); positive FAB-MS: m/z: 1903 $[M-2PF_6]^{2+}$; positive ESI-MS: m/z: 1903 $[M-2PF_6]^{2+}$; ^{1}H NMR (300 MHz, CD_2Cl_2, 298 K): $\delta = 0.04$ (m, 12H, CH_3), 0.27 (m, 4H, CCH_2C), 0.85 (m, 4H, CCH_2C), 2.33 (m, 4H, NCH_2), 2.80 (m, 4H, NCH_2), 6.83 (m, 8H, Ph), 7.12–7.83 (m, 72H, Ph); ^{31}P{^{1}H} NMR (202 MHz, CD_2Cl_2, 298 K): $\delta = 83.1, 85.5$ (dd, $J_{P,P} = 115$ Hz); molar conductivity (acetone, 298 K): $\Lambda_M = 262\ \Omega^{-1}\,cm^2\,mol^{-1}$ (1:2 electrolyte).

[11] a) Crystal data for **1**: $Au_{10}S_4(C_{27}H_{27}P_2N)_4 \cdot 2PF_6$, $M_r = 4097.59$, tetragonal, space group $I\bar{4}$ (no. 82), $a = 18.9950(14)$, $c = 17.7282(19)$ Å, $V = 6396.5(10)$ Å^3, $Z = 2$, $\rho_{calcd} = 2.127$, $\mu(Mo_{K\alpha}) = 11.670\ mm^{-1}$, $F(000) = 3792$, $T = 293$ K; $R = 0.0347$, $wR = 0.0870$ for 7314 reflections with $I > 2\sigma(I)$. Crystal dimensions $0.20 \times 0.14 \times 0.12$ mm; Bruker CCD area detector diffractometer, $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å); collection range $2\theta = 3-55°$; Phi and Omega oscillation frames 0–180°; 1321 frames taken in four shells. Absorption correction applied by using the program SADABS[11b]; the structure was determined by direct methods and subsequent difference Fourier syntheses, and refined by full-matrix least-squares on F^2 by using the programs of the Bruker Smart and Bruker Shelxtl package[11b]. All non-hydrogen atoms were refined anisotropically. Crystallographic data (excluding structure factors) for the structure reported in this paper has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-138838. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).; b) SADABS, Bruker Smart and Bruker Shelxtl Package, Bruker AXS GmbH, **1998**.

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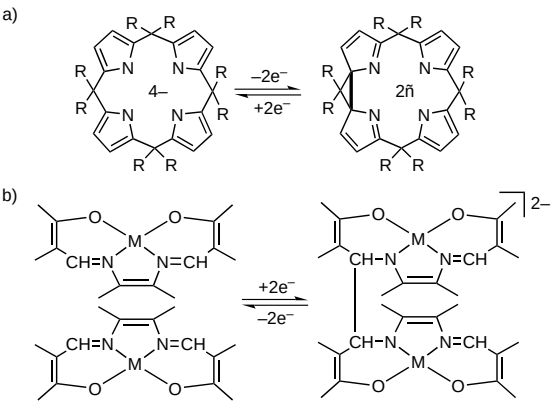
Metal-Mediated Transfer of Electrons between Two Different C–C Single Bonds That Function as Electron-Donor and Electron-Acceptor Units**

Federico Franceschi, Euro Solari, Rosario Scopelliti, and Carlo Floriani*

Two complementary electron-storage and -releasing units are the fundamental constituents of storage cells[1] and molecular devices devoted to long-range electron-transfer processes.[2] The C–C single bonds formed by oxidative (Scheme 1a)[3] or reductive coupling[4] (Scheme 1b) can be



Scheme 1. Reversible two-electron oxidative (a) and reductive coupling (b) to form C–C bonds. R = Et.

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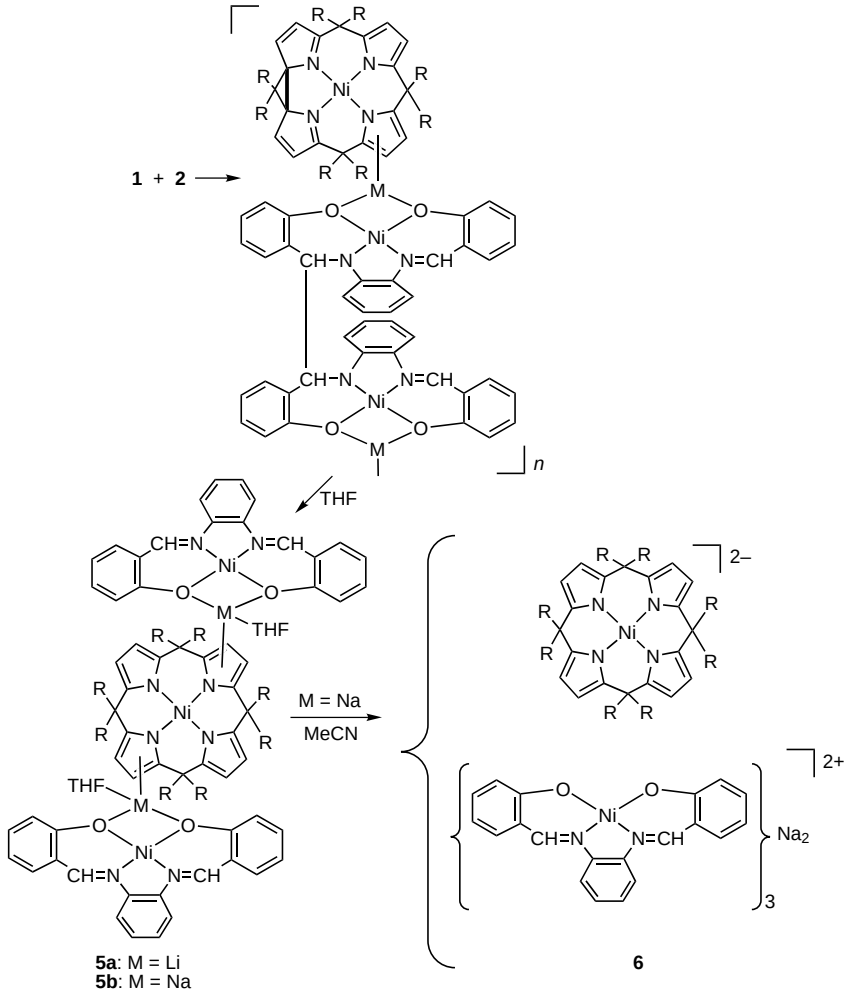
used for storing and releasing pairs of electrons in a reversible manner.

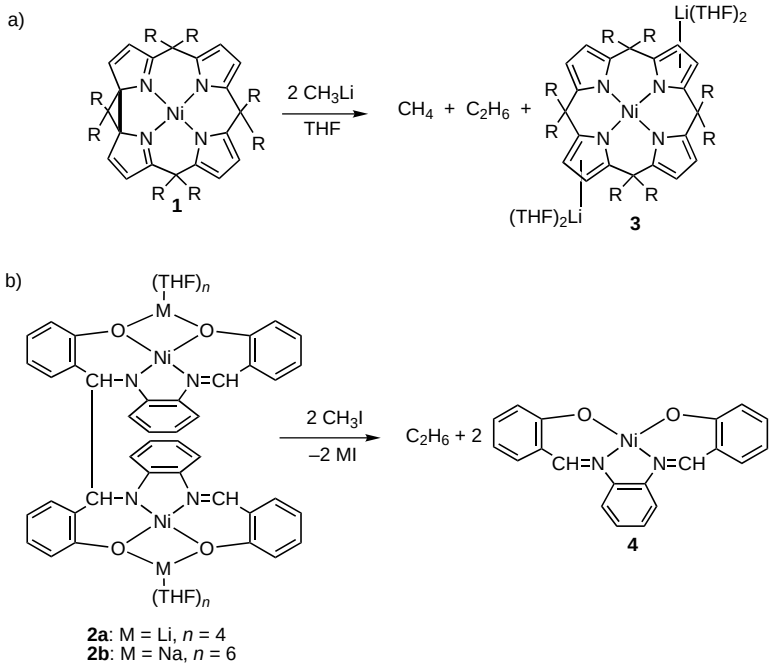
The novelty of the system reported here lies in the nature of the electron-storage and -release units, both of which are ubiquitous C–C single bonds, and on how the communication between them is mediated by metal ions. In addition, the two complementary C–C units operate without being involved, at any stage, in chemical reactions.

Redox chemistry involving exclusively C–C single bonds was investigated for complexes **1**, **2a**, and **2b**, and the complementary behavior of the two different C–C bonds was demonstrated. Although the two complementary systems are chemically quite different, they both bind alkali metal cations at the periphery.[5, 6] They form tight ion-pair structures, in which the pyrrolyl anions or the Schiff base oxygen atoms, respectively, function as binding sites for the alkali metal cations. The oxidizing properties of **1** were demonstrated, among others, in its reaction with LiMe,[7] which led to the expected evolution of a mixture of CH_4 and C_2H_6 and the cleavage of the cyclopropane unit (Scheme 2). The partner reaction of **2a** or **2b** with CH_3I[7] also resulted in the formation of C_2H_6 and cleavage of the C–C bond across the two salophen units, whereby the C–C bond functioned as a two-electron donor.

The complementarity of the two processes was then proved by adding a solution of **2a** or **2b** in THF to a solution of **1** in THF, which led to immediate precipitation of **5a** or **5b**, respectively (Scheme 3). The latter was recovered as the ion-separated compound **6**[8] under the crystallization conditions, rather than in the ion-pair form. The crystal structure of **6** is shown in Figure 1[9].



Scheme 3. Electron transfer system between electron-rich and electron-poor C–C bonds assisted by alkali metal ions.



Scheme 2. A C–C bond functioning as a two-electron oxidizing (a) and reducing agent (b).

The occurrence of intermolecular electron transfer and the nature of the final compound emphasizes the assistance of both the central transition metal ion and the alkali metal ion in the redox process. The chemical transformation displayed in Scheme 3 could be exploited for energy storage (e.g., storage cells) or transfer. Although for both model compounds, **2** and **1**, the C–C bond is the site of storage or deficiency, respectively, of a pair of electrons, these functional groups are not involved in any chemical reactions; the metal atom assists electron transfer from the C–C bond to the substrate.[4e, f] This chemical behavior ensures complete chemical and energetic reversibility of the system. Apart from the practical applicability of this system, the novel concept of exploiting ubiquitous C–C bonds for energy-storing and electron-transfer processes is noteworthy.

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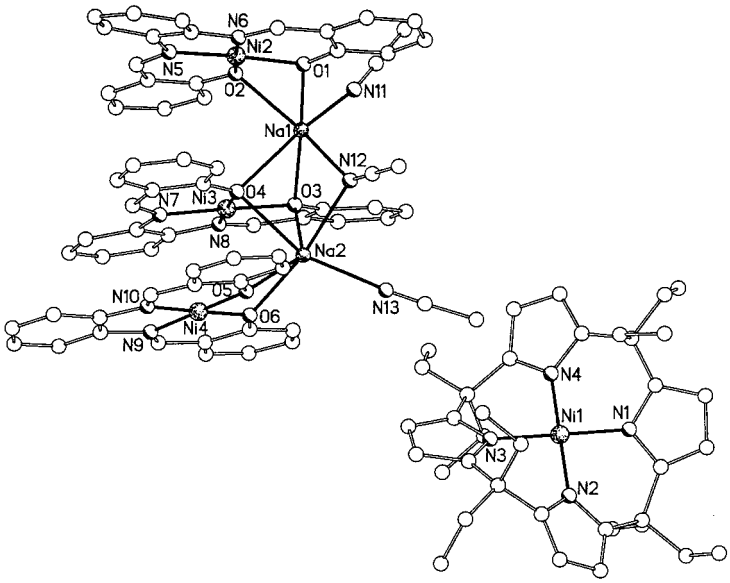

Figure 1. Crystal structure of **6** (hydrogen atoms and interstitial CH_3CN solvent molecules omitted for clarity).

Experimental Section

1: A solution of iodine (3.21 g, 12.7 mmol) in THF (100 mL) was added dropwise to a solution of $[NiEt_8Py_4Na_2]\cdot 2Et_2O$[7] (10 g, 12.7 mmol; Py = pyrrolyl) in THF (100 mL). The resulting red suspension was stirred for 12 h and then concentrated to dryness. The residue was extracted with CH_2Cl_2 (60 mL) to give a suspension from which a red microcrystalline solid was collected and dried in vacuo (5.97 g, 79 %). Elemental analysis calcd for $C_{36}H_{48}N_4Ni$: C 72.61, H 8.12, N 9.41; found: C 72.58, H 8.05, N 9.23; ^{1}H NMR (400 MHz, [D$_6$]benzene, 298 K): $\delta = 6.67$ (d, $J = 5.1$ Hz, 2H, CH), 6.53 (d, $J = 2.7$ Hz, 2H, CH), 6.32 (d, $J = 2.7$ Hz, 2H, CH), 6.11 (d, $J = 5.1$ Hz, 2H, CH), 3.57 (q, $J = 7.0$ Hz, 2H, CH_2), 2.87 (q, $J = 7.4$ Hz, 2H, CH_2), 2.50 (q, $J = 7.2$ Hz, 2H, CH_2), 2.28 (m, 2H, CH_2), 1.84 (m, 4H, CH_2), 1.69 (q, $J = 6.8$ Hz, 2H, CH_2), 1.31 – 1.18 (m, 8H, CH_2, CH_3), 1.02 (t, $J = 7.0$ Hz, 3H, CH_3), 0.88 (m, 6H, CH_3), 0.70 (m, 6H, CH_3), 0.48 (t, $J = 6.85$ Hz, 3H, CH_3); ^{13}C NMR (100.6 MHz, [D$_6$]benzene, 298 K): $\delta =$ 147.6, 139.3, 130.7, 130.0, 104.5, 104.0, 85.8, 67.1, 57.7, 51.8, 47.5, 44.8, 39.3, 33.3, 30.0, 27.9, 25.1, 11.2, 11.1, 11.0, 10.7, 10.3, 10.1.

5a: A red solution of **1** (0.75 g, 1.26 mmol) in THF (50 mL) was added to a dark green suspension of **2a**[4a] (1.32 g, 1.26 mmol) in THF (50 mL). A brown-red precipitate separated immediately from the resulting brown solution. The suspension was stirred for 12 h then the solid was collected and dried in vacuo (1.41 g, 75 %). Elemental analysis calcd for **5a**, $C_{84}H_{92}Li_2N_8Ni_3O_6$: C 65.87, H 6.05, N 7.31; found: C 65.38, H 5.75, N 7.30. IR (Nujol): $\tilde{\nu} = 1606$ (s), 1578 (s) 1534 (s), 1488 (m), 1444 (s), 1326 (s), 1262 (w), 1196 (s), 1152 (m), 1129 (m), 1068 (w), 1042 (m), 950 (w), 929 (m), 880 (w), 840 (w), 813 (m), 747 (s), 735 (s), 721 (m), 700 (m), 622 (w), 570 (w), 547 (m), 507 (w), 450 (w), 408 cm^{-1} (w).

5b and **6**: A red solution of **1** (0.87 g, 1.46 mmol) in THF (100 mL) was added to a dark green solution of **2b**[4a] (1.79 g, 1.46 mmol) in THF (100 mL). A red precipitate separated immediately from the resulting dark orange-red solution. The suspension was stirred overnight then the solid was collected and dried in vacuo (1.81 g, 81 %). Elemental analysis calcd for **5b**, $C_{84}H_{92}N_8Na_2Ni_3O_6$: C 65.87, H 6.05, N 7.31; found: C 65.38, H 5.75, N 7.30. IR (Nujol): $\tilde{\nu} = 1608$ (s), 1578 (s), 1527 (s), 1483 (s), 1356 (m), 1330 (s), 1317 (s), 1286 (s), 1258 (m), 1235 (w), 1193 (s), 1151 (s), 1129 (m), 1053 (w), 1025 (w), 929 (m), 901 (w), 871 (w), 848 (w), 808 (w), 755 (s), 744 (s), 713 (s), 649 (w), 612 (w), 584 (w), 565 (s), 545 (s), 483 (w), 452 (m), 410 cm^{-1} (m). The product was recrystallized from acetonitrile to give deep red crystals of **6** that were suitable for X-ray analysis. The crystals were collected, dried in vacuo, and analyzed. Elemental analysis calcd for $\mathbf{6}\cdot CH_3CN$, $C_{98}H_{93}N_{11}Na_2Ni_4O_6$: C 65.33, H 5.20, N 8.55; found: C 65.23, H 4.65, N 8.38.

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[7] For experimental details see Supporting Information.

[8] In such complexes, the ligand distribution often gives rise to the least soluble complex in the solid state; hence, the [Ni(salophen)]/Na ratio is 3:2 rather than 1:1.[4, 6]

[9] Crystal structure analysis of **6**: $[C_{66}H_{51}N_9Na_2Ni_3O_6][C_{36}H_{48}N_4Ni]\cdot 3C_2H_3N$, $M_r = 2006.92$, orthorhombic, space group $Pna2_1$, $a = 20.868(3)$, $b = 21.738(3)$, $c = 20.9686(14)$ Å, $V = 9512.0(19)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.401$ g cm^{-3}, $F(000) = 4200$, $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), $\mu(Mo_{K\alpha}) = 0.855$ mm^{-1}; crystal dimensions $0.20 \times 0.14 \times 0.10$. For 13108 observed reflections ($I > 2\sigma(I)$) and 1227 parameters, the conventional R is 0.0926 ($wR2 = 0.1572$ for 15798 independent reflections). Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-137426. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).