stability as well as the temperature for the replacement of ethylene follows the same order as the shielding of the cobalt nucleus.

Conclusion

It has been shown that despite of their large line width, the large shift range of ^{59}Co resonances in organocobalt complexes enables relevant chemical information to be obtained from ^{59}Co NMR spectra. In organocobalt(I) complexes with π-ligands $\delta(^{59}\mathrm{Co})$ seems to be governed by the paramagnetic shielding term and its $1/\Delta E$ dependence. The ^{59}Co shielding then can be rationalized by changes of the energy gap between the frontier levels of the complexes when olefins of variable donor and acceptor properties are bound to CpCo. Within this concept $\delta(^{59}\mathrm{Co})$ may be used as an indication of relative chemical stability, at least within a series of closely related compounds.

Registry No. **1**, 12082-45-0; **2**, 12295-18-0; **3**, 86900-89-2; **4**, 94792-00-4; **5**, 94791-96-5; **6**, 69393-67-5; **7**, 98704-25-7; **8**, 98704-26-8; **9**, 12184-35-9; **10**, 98704-27-9; **11**, 98704-28-0; **12**, 98704-29-1; **13**, 98704-30-4; **14**, 84180-58-5; **15**, 34829-55-5; **16**, 98704-31-5; **17**, 98704-32-6; **18**, 80848-36-8; **19**, 88228-63-1; **20**, 84180-59-6; **21**, 98704-33-7; **22**, 1271-08-5; **23** (isomer 1), 98704-34-8; **23** (isomer 2), 98757-91-6; **24**, 98704-35-9; **25**, 93058-42-5; **26**, 98704-36-0; **27**, 98704-37-1; **28**, 98704-38-2; **29**, 33032-03-0; **30**, 98704-39-3; **31**, 79160-70-6; **32**, 94791-70-5; **33**, 38959-22-7; **34**, 98704-40-6; **35**, 55518-03-1; **36**, 86900-88-1; **37**, 98704-41-7; **38**, 98704-42-8; **39**, 98704-43-9; **40**, 70210-70-7; **41**, 78318-94-2; **42**, 77070-14-5; **43**, 98704-44-0; **44**, 98704-45-1; **45**, 98704-46-2; **46**, 12078-25-0; ^{59}Co, 7440-48-4.

Communications

Stereochemical and Electrochemical Analyses of the Cyclopentadienyl and Methylcyclopentadienyl Dinitrosyl-Capped Tricobalt Analogues, $Co_3(\eta^5\text{-}C_5H_{5-x}Me_x)_3(\mu_3\text{-}NO)_2$ (Where $x = 0, 1$), of the Classical Fischer–Palm $Ni_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}CO)_2$

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Summary: The slow addition of $Co(\eta^5\text{-}C_5H_5)(CO)_2$ to a photolyzed THF solution of the Fe–Fe double-bonded $Fe_2(\eta^5\text{-}C_5H_5)_2(\mu_2\text{-}NO)_2$ unexpectedly afforded $Co_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}NO)_2$ (**1**) in 3–5% yield. This 48-electron cluster (previously isolated and spectroscopically characterized) and its methylcyclopentadienyl derivative (**2**) were found from single-crystal X-ray diffraction analyses to possess analogous $Co_3(NO)_2$ cores of D_{3h}—$3/m2m$ geometry (exact for **1** and ideal for **2**). Both **1** and **2** were shown from CV measurements to possess similar reversible electron-transfer properties with each neutral parent undergoing a one-electron oxidation to its 47-electron monocation and a one-electron reduction to its 49-electron monoanion.

As a part of our research involving the rational synthesis of triangular metal clusters with triply bridging nitrosyl ligands[2,3] via metal fragment addition to the Fe–Fe double-bonded $Fe_2(\eta^5\text{-}C_5H_5)_2(\mu_2\text{-}NO)_2$,[4] a photochemical reaction of the iron nitrosyl dimer with $Co(\eta^5\text{-}C_5H_5)(CO)_2$ was carried out. The anticipated cycloaddition product, the (as yet) unknown $Fe_2Co(\eta^5\text{-}C_5H_5)_3(CO)(NO)_2$ which is an isolobal analogue of $Co_3(\eta^5\text{-}C_5H_5)_3(CO)_3$,[5] was not obtained; instead, this reaction gave a small quantity of $Co_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}NO)_2$ (**1**). This cobalt–dinitrosyl 48-electron analogue of the classical Fischer–Palm 49-electron $Ni_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}CO)_2$[6] was originally prepared by Müller and Schmidt[7] via the thermolysis of $Co_2(\eta^5\text{-}C_5H_5)_2(\mu_2\text{-}NO)_2$ in THF and was characterized by them from ^{1}H NMR, IR, and mass spectral data. In light of our structural-bonding-electrochemical investigations of the interrelated $[Ni_3(\eta^5\text{-}C_5H_{5-x}Me_x)_3(\mu_3\text{-}CO)_2]^n$ series ($x = 0, 1, 5$; $n = 1+, 0, 1-$),[6] the corresponding $[(\eta^5\text{-}C_5Me_5)CoNi_2(\eta^5\text{-}C_5H_5)_2(\mu_3\text{-}CO)_2]^n$ series ($n = 0, 1-$)[6c,d] the $[Co_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}CO)_2]^n$ series ($n = 0, 1-$),[8] the $[Co_3(\eta^5\text{-}C_5H_{5-x}Me_x)_3(\mu_3\text{-}CO)(\mu_3\text{-}NH)]^n$ series ($x = 0, 1$; $n = 2+, 0, 2-$),[9] and the $[Co_3(\eta^5\text{-}C_5H_4Me)_3(\mu_3\text{-}NO)(\mu_3\text{-}NH)]^n$ series ($n = 1+, 0$)[9], we presumed that 1 should also possess reversible redox behavior. Herein are presented the X-ray crystallographic

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(1) On leave (Sept 1983–Feb 1984) at UW—Madison from School of Chemistry, University of New South Wales, Kensington, New South Wales 2033, Australia.

(2) Kubat-Martin, K. A.; Rae, A. D.; Dahl, L. F. "*Abstracts* of Papers", 187th National Meeting of the American Chemical Society St. Louis, MO, Apr 1984; American Chemical Society: Washington, D.C., 1984.

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(6) (a) $Ni_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}CO)_2$ (synthesis): Fischer, E. O.; Palm, C. *Chem. Ber.* **1958**, *91*, 1725–1731. (b) $Ni_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}CO)_2$ (X-ray data): Hock, A. A.; Mills, O. S. In "Advances in the Chemistry of Coordination Compounds"; Kirschner, S., Ed.; Macmillan: New York, 1961; pp 640–648. (c) $Ni_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}CO)_2$ (X-ray data) and $(\eta^5\text{-}C_5H_{5-x}Me_x)CoNi_2(\eta^5\text{-}C_5H_5)_2(\mu_3\text{-}CO)_2$ (where $x = 0, 1, 5$) (synthesis, X-ray data, CV): Byers, L. R.; Uchtman, V. A.; Dahl, L. F. *J. Am. Chem. Soc.* **1981**, *103*, 1942–1951. (d) $[Ni_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}CO)_2]^-$, $[Ni_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}CO)_2]^n$ (where $n = 2+, 1+, 0, 1-$), and $[(\eta^5\text{-}C_5Me_5)CoNi_2(\eta^5\text{-}C_5H_5)_2(\mu_3\text{-}CO)_2]^-$: Maj, J. A.; Rae, A. D., Dahl, L. F. *J. Am. Chem. Soc.* **1982**, *104*, 3054–3063. (e) $Ni_3(\eta^5\text{-}C_5H_4Me)_3(\mu_3\text{-}CO)_2$ (synthesis, X-ray data): Englert, M. L.; Dahl, L. F., to be submitted for publication. (f) $[Ni_3(\eta^5\text{-}C_5H_{5-x}Me_x)_3(\mu_3\text{-}CO)_2]^n$ (where $x = 0, 1$; $n = 1+, 0, 1-$) (CV): Bedard, R. L.; Dahl, L. F., submitted for publication.

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0276-7333/85/2304-2221$01.50/0

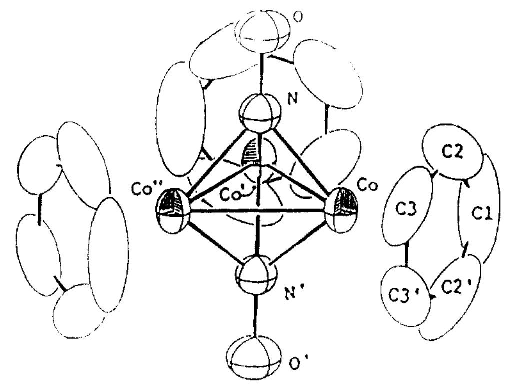

Figure 1. Molecular configuration of $Co_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}NO)_2$ (1). This 48-electron structural analogue of the Fischer–Palm 49-electron $Ni_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}CO)_2$ cluster also possesses crystallographic C_{3h}—$3/m$ site symmetry with each cyclopentadienyl ring having a twofold orientational disorder of half-weighted atoms (with only one orientation shown).

results and electrochemical properties of both 1 and its methylcyclopentadienyl derivative, $Co_3(\eta^5\text{-}C_5H_4Me)_3(\mu_3\text{-}NO)_2$ (2). Our initial goal was to establish the electron-transfer properties of 1 and 2 as well as to determine the architectural variations brought about by the formal replacement of carbonyl ligands with nitrosyl ligands. The existence of only a few triangular metal clusters with triply bridging nitrosyl ligands coupled with the recent discoveries that the triply bridging nitrosyl ligands in both $Mn_3(\eta^5\text{-}C_5H_4Me)_3(\mu_3\text{-}NO)(\mu_2\text{-}NO)_3$[10] and the isolobal $(\eta^5\text{-}C_5H_4Me)MnFe_2(\eta^5\text{-}C_5H_5)_2(\mu_3\text{-}NO)(\mu_2\text{-}NO)(\mu_2\text{-}CO)_2$[3] undergo N–O bond cleavage transformations (without molecular rearrangement) to give N–H ligands provided a further incentive to explore the chemical–electrochemical reactivity of 1 and 2.

The Müller–Schmidt cluster (1) was prepared by a photolytic reaction involving the addition over several hours of an equimolar quantity of $Co(\eta^5\text{-}C_5H_5)(CO)_2$ (in THF) to $Fe_2(\eta^5\text{-}C_5H_5)_2(\mu_2\text{-}NO)_2$ (also in THF) which was photolyzed with a 450-W Hanovia Hg vapor lamp. After a 60-h photolysis, separation of the products on an alumina column (toluene/THF) gave, in addition to $Fe_2(\eta^5\text{-}C_5H_5)_2(\mu_2\text{-}CO)_2(CO)_2$ as the major product, 1 (in 3–5% yield) and starting materials (along with non-identified, insoluble species). The identity of 1 was established via IR, ^1H NMR, and mass spectra[11] and substantiated by an X-ray crystallographic determination[12,13] of its molecular structure. In subsequent work 1 was prepared by the much higher yielding Müller-Schmidt procedure.[7] The corresponding synthesis and characterization[14-16] of the methylcyclopentadienyl analogue (2) were undertaken in order to provide a structural–electrochemical comparison with 1.

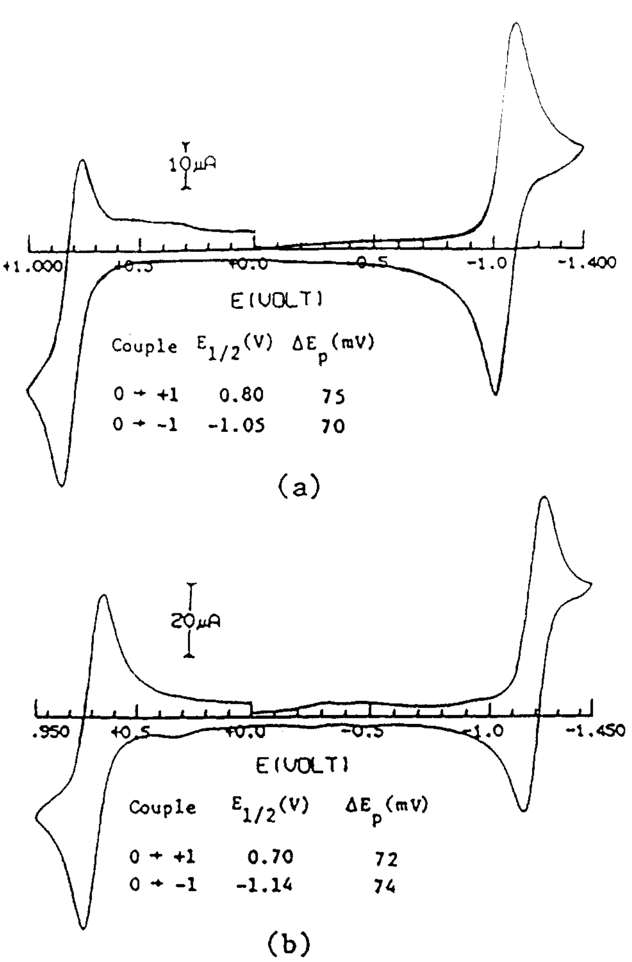

Figure 2. Cyclic voltammograms of (a) $Co_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}NO)_2$ (1) and (b) $Co_3(\eta^5\text{-}C_5H_4Me)_3(\mu_3\text{-}NO)_2$ (2). Each CV was carried out in CH_2Cl_2/0.1 M$[NBu_4]^+[PF_6]^-$ at a platinum disk electrode with a scan rate of 200 mV/s.

The overall molecular configuration of 1 is given in Figure 1. The crystallographic requirement for 1 of C_{3h}—$3/m$ site symmetry results in the $Co_3(NO)_2$ core conforming to D_{3h}—$3/m2m$ symmetry with each cyclo-

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[10] Legzdins, P.; Nurse, C. R.; Rettig, S. J. *J. Am. Chem. Soc.* **1983**, *105*, 3727-3728.

[11] A solid-state IR spectrum (KBr pellet) displayed a single nitrosyl band at 1400 (m) cm^{-1}. A ^1H NMR spectrum ($CDCl_3$) exhibited a sharp proton resonance at δ 4.77. A mass spectrum (electron impact, 15 eV) showed the existence of the parent ion peak with other prominent peaks assigned to the $[Co_3(C_5H_5)_3(NO)]^+$ fragment (m/e 402) and the $[Co(C_5H_5)_2]^+$ fragment (m/e 189). These spectral data are in close agreement with those reported by Müller and Schmidt.[7]

[12] $Co_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}NO)_2$ (fw = 431.80): black hexagonal-shaped crystals (0.2 × 0.25 × 0.3 mm) obtained by slow diffusion of hexane into a THF solution containing the cluster; hexagonal $P6_3/m$ (C^2_{6h}— no. 176); $a = b = 9.143$ (7) Å, $c = 10.507$ (9) Å, $V = 760$ (1) Å^3; $D_{calcd} = 1.89$ g/cm^3 for $Z = 2$; linear absorption coefficient $\mu = 32.4$ cm^{-1} for Mo Kα radiation; empirical absorption correction made (Rae, A. D., submitted for publication). The crystal structure was determined from a Patterson function followed by successive Fourier syntheses. Least-squares refinement (RAELS[13]) converged at $R_1(F) = 4.4\%$ and $R_2(F) = 5.0\%$ for 246 independent data [$I > 3\sigma(I)$] obtained at room temperature via a Syntex (Nicolet) P$\bar{1}$ diffractometer with Mo Kα radiation.

[13] Rae, A. D. RAELS, "A Comprehensive Least-Squares Program"; University of New South Wales, Kensington, 1976; adapted for a Harris/7 computer by A. D. Rae, University of Wisconsin—Madison, 1984.

[14] As expected, the methylcyclopentadienyl 2 is much more soluble than 1 in organic solvents (e.g., CH_2Cl_2, $CHCl_3$, and THF), in each of which dissolution of the black crystals of 2 likewise produces a dark red solution. The thermal stability of 2 is evidenced by its nonreactivity in refluxing octane solution (126 °C). An IR spectrum of 2 in THF showed three sharp bands in the triply bridging nitrosyl region at 1401 (vs), 1379 (s), and 1363 (m) cm^{-1}; in CH_2Cl_2 the IR spectrum of 2 consisted of an equal-intensity, three-band pattern at 1390 (s), 1373 (s), and 1359 (s) cm^{-1}. A solid-state IR spectrum (KBr pellet) of 2 exhibited three bands at 1401 (vs), 1376 (s), and 1361 (s) cm^{-1}. A ^1H NMR spectrum of 2 in $CDCl_3$ displayed two equivalent sets of cyclopentadienyl ring proton resonances at δ 4.56 (6 H) and 4.51 (6 H) and a single methyl proton resonance at δ 1.76 (9 H). The presence in 2 of three IR bands in the nitrosyl-bridging region is attributed to the existence of conformational isomers of 2 corresponding to the three C_5H_4Me ligands possessing more than one set of orientations.

[15] $Co_3(\eta^5\text{-}C_5H_4Me)_3(\mu_3\text{-}NO)_2$ (fw = 473.80): black parallelepiped-shaped crystals (0.1 × 0.2 × 0.2 mm) obtained by slow diffusion of hexane into a THF solution containing the cluster; triclinic, $P\bar{1}$ (C^1_i— no. 2); $a = 9.049$ (7) Å, $b = 12.313$ (17) Å, $c = 8.962$ (6) Å, $\alpha = 101.13$ (9)°, $\beta = 118.09$ (5)°, $\gamma = 84.75$ (9)°, $V = 864$ (2) Å^3; $D_{calcd} = 1.82$ g/cm^2 for $Z = 2$; linear absorption coefficient $\mu = 28.6$ cm^{-1} for Mo Kα radiation; empirical absorption correction made (Rae, A. D., submitted for publication). The crystal structure was determined by direct methods (MULTAN[16]) and refined by least-squares (RAELS[13]) to $R_1(F) = 4.77\%$ and $R_2(F) = 7.85\%$ for 2685 independent data [$I > 3\sigma(I)$] obtained at -60 °C with a Syntex P$\bar{1}$ diffractometer with Mo Kα radiation.

[16] Germain, G.; Main, P.; Woolfson, M. M. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1971**, *A27*, 368-376.

pentadienyl ring possessing a twofold rotational disorder. The geometry of the $Co_3(NO)_2$ core in 2, which has C_1—1 site symmetry, is essentially the same as that of 1, as shown from a bond-length comparison—viz., the independent Co–Co distance of 2.399 (3) Å in 1 vs. three Co–Co distances of range 2.395 (1)–2.414 (1) Å (mean, 2.403 Å) in 2 and the independent Co–NO distance of 1.843 (9) Å in 1 vs. six Co–NO distances of range 1.856 (4)–1.873 (4) Å (mean, 1.863 Å) in 2. The mean Co–Co bond lengths in 1 and 2 are significantly longer than that of 2.370 (1) Å in the 46-electron $Co_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}CO)_2$[8] but are virtually identical with those in other sterically uncrowded, 48-electron bicapped tricobalt clusters with either carbon- or nitrogen-attached atoms (of similar size)—e.g., the $[Co_3(\eta^6\text{-}C_6H_6)_3(\mu_3\text{-}CO)_2]^+$ monocation (2.399 Å)[17] as the $[BPh_4]^-$ salt, $Co_3(\eta^5\text{-}C_5H_4Me)_3(\mu_3\text{-}CO)(\mu_3\text{-}NC(O)NH_2)$ (2.400 Å),[9] and the $[Co_3(\eta^5\text{-}C_5H_4Me)(\mu_3\text{-}NO)(\mu_3\text{-}NH)]^+$ monocation (2.406 Å)[9] as the $[BPh_4]^-$ salt. The Co–NO bond lengths in 1 and 2 are comparable to those in the 48-electron $[Co_3(\eta^5\text{-}C_5H_4Me)_3(\mu_3\text{-}NO)(\mu_3\text{-}NH)]^+$ monocation (mean 1.869 Å)[9] but are considerably smaller than the corresponding Co–CO bond lengths in the 46-electron $Co_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}CO)_2$ (1.951 (6) Å)[8] and in the 48-electron $Co_3(\eta^5\text{-}C_5H_4Me)_3(\mu_3\text{-}CO)(\mu_3\text{-}NC(O)NH_2)$ (mean, 1.930 Å).[9] The shorter Co–NO bond lengths are likely due to the greater electron π-acceptor ability of the triply bridging nitrosyl ligand (relative to a triply bridging carbonyl ligand) in these clusters.

Cyclic voltammetric measurements[18] (Figure 2) revealed that 1 and 2 have similar reversible redox behavior with each CV displaying a one-electron oxidation couple to the 47-electron monocation and a one-electron reduction couple to the 49-electron monoanion. The designation of each redox couple as a one-electron process is based upon the equivalent peak current heights of the oxidation and reduction couples in 1 and in 2 together with an equimolar mixture of 2 and $[Co_3(\eta^5\text{-}C_5H_4Me)_3(\mu_3\text{-}NO)(\mu_3\text{-}NH)]^+[BPh_4]^-$ (which was independently shown[9] to have a reversible one-electron reduction couple) exhibiting equivalent peak current heights for the two reduction couples. A comparative analysis of the corresponding $E_{1/2}$ values between 1 and 2 shows that 2 is easier to oxidize (by 0.10 V) but more difficult to reduce (by 0.09 V) than 1; this trend is consistent with the enhanced electron donating ability of the C_5H_4Me ligands (relative to the C_5H_5 ligands) which gives rise to increased electron density at the cobalt atoms and hence to higher energies for both the HOMO (from which one electron is removed upon oxidation) and LUMO (to which one electron is added upon reduction).

Work in our laboratories is currently directed at the following: (1) isolation of the oxidized 47-electron and reduced 49-electron species of 1 and 2 for spectroscopic and structural characterization to determine the redox-generated changes in geometry; and (2) protonation and alkylation reactions of the neutral parents (1 and 2) involving possible N–O bond-cleavage transformations.

Acknowledgment. This research was supported by the National Science Foundation. We are especially grateful to Dr. R. B. Cody (Nicolet Analytical Instruments) for obtaining a mass spectrum of 1 with a Nicolet FT-MS 1000 mass spectrometer. Special thanks are also due to Dr. Robert L. Bedard for helpful suggestions in carrying out the electrochemical measurements.

Registry No. 1, 58071-54-8; 2, 98689-82-8; $Fe_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}NO)_2$, 52124-51-3; $Co(\eta^5\text{-}C_5H_5)(CO)_2$, 12078-25-0; $Fe_2Co(\eta^5\text{-}C_5H_5)_3(CO)(NO)_2$, 98689-81-7; $Ni_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}CO)_2$, 12194-69-3; $Fe_2(\eta^5\text{-}C_5H_5(\mu\text{-}CO)_2(CO)_2$, 12154-95-9; $Co_2(\eta^5\text{-}C_5H_4Me)_2(\mu\text{-}NO)_2$, 85454-64-4.

Supplementary Material Available: Six tables listing the atomic parameters, intramolecular distances and bond angles, and the observed and calculated structure factor amplitudes for both $Co_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}NO)_2$ (1) and $Co_3(\eta^5\text{-}C_5H_4Me)_3(\mu_3\text{-}NO)_2$ (2) (33 pages). Ordering information is given on any current masthead page.

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(17) Olson, W. L.; Dahl, L. F., submitted for publication.

(18) Cyclic voltammetric data were obtained with a BAS-100 Electrochemical Analyzer with the electrochemical cell enclosed in a N_2-filled Vacuum Atmospheres drybox. The working electrode was a platinum disk; the reference electrode was a vicor-tipped, aqueous SCE separated from the test solution by a vicor-tipped salt bridge filled with a 0.1 M $TBAPF_6/CH_3CN$ solution. The counterelectrode was a platinum coil. Solution volumes were about 5 mL of CH_2Cl_2 with an approximate concentration of 10^{-3} M of cluster compound.

Diethyl Ether Adducts of Bis(pentamethylcyclopentadienyl)europium(II) and -ytterbium(II): Excited-State Energy Transfer with Organolanthanoid Complexes

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Summary: The title compound $(\eta^5\text{-}Me_5C_5)_2Eu^{II}\cdot OEt_2$, **1**, exhibits photoluminescence (uncorrected $\lambda_{max} \approx 730$ nm) at 295 K in toluene solution; a radiative quantum yield of ~0.04 and lifetime of ~400 ns were measured for **1** under these conditions. Quenching of the emission from **1** by $(\eta^5\text{-}Me_5C_5)_2Yb^{II}\cdot OEt_2$, **2**, in toluene solution demonstrates energy transfer between two organolanthanoid complexes. A Stern–Volmer treatment of the quenching of the emission intensity and lifetime of **1** yields a bimolecular quenching rate constant of $\sim 7 \times 10^8$ M^{-1} s^{-1}.

Recent studies of organolanthanoid complexes have demonstrated that photoluminescence can be observed at 295 K from a variety of Yb(III),[1] Tb(III),[2] and Yb(II),[3,4] adducts possessing cyclopentadienyl ligands or derivatives thereof. We report in this communication that a Eu(II) organolanthanoid complex, $(\eta^5\text{-}Me_5C_5)_2Eu^{II}\cdot OEt_2$, 1, emits at room temperature. Moreover, photoluminescence from 1 can be quenched in toluene solution by energy transfer to $(\eta^5\text{-}Me_5C_5)_2Yb^{II}\cdot OEt_2$, 2. To our knowledge, this is the first example of excited-state energy transfer involving two organolanthanoid complexes.

Compound 1[5] is a red-brown solid which yields bright red photoluminescence at 295 K when excited with visible or near-UV light. Toluene solutions of 1 are reddish brown

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(2) Brittain, H. G.; Meadows, J. H.; Evans, W. J. *Organometallics* **1983**, 2, 1661.

(3) Thomas, A. C.; Ellis, A. B. *J. Chem. Soc., Chem. Commun.* **1984**, 1270.

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