

Figure 1. Resonance Raman spectra of C_{60} and C_{60}^- in oxygen-free (70%/30%) toluene/acetonitrile solvent. Spectra were recorded using 20-mW 356.4-nm (Kr^+) excitation. The sample was stirred continuously in a cell designed for simultaneous Raman/absorption measurements.⁶ Asterisks (*) designate solvent modes.

cm^{-1} in a film of composition K_3C_{60} , which is highly conducting, and becomes superconducting below 18 K.¹ At the composition K_6C_{60} , the film is an insulator, reflecting the complete filling of the t_{1u} LUMO, and the vibrational frequency is 1430 cm^{-1} . These numbers indicate a frequency shift of $6\text{--}7\text{ cm}^{-1}$ per added electron, and indeed a C_{60}^- salt, $[(Ph_4As^+C_{60}^-) \cdot 2(Ph_4As^+Cl^-)]$, was found to show a 6 cm^{-1} shift of the pentagonal pinch mode relative to the undoped C_{60} film.¹

In contrast, surface enhanced Raman scattering (SERS) studies of C_{60} deposited on gold and silver surfaces show variable results depending upon the metal substrate and the counterion employed.^{3-5,10} Garrell and co-workers³ observed a shift in the pentagonal pinch mode at a gold electrode in KCl electrolyte from 1452 to 1444 cm^{-1} upon changing the electrode potential from 0.0 to -0.6 V vs SCE. Weaver and co-workers⁴ report a shift in the same mode at a gold electrode in tetrabutylammonium perchlorate electrolyte from 1461 to 1443 cm^{-1} at an applied potential of -1.0 V (vs Fc^+/Fc), where voltammetry shows reduction of C_{60} to the monoanion. This shift is 3 times as large as expected on the basis of the film doping data. If addition of an electron shifts the pentagonal pinch frequency by as much as 18 cm^{-1} , then the degree of electron transfer to C_{60} in doped films would appear to be much less than one per potassium atom. An alternative interpretation of the discrepancy, however, is that the larger SERS shift is due to perturbation of the C_{60} monoanion by interactions at the gold surface or to counterion effects in the C_{60} film. (We have recently learned¹⁰ that the downshift to the pentagonal pinch SERS band upon reduction of C_{60} surface films is highly sensitive to the counterion in the supporting electrolyte.)

To resolve this issue we undertook to determine the shift in the pentagonal pinch frequency upon controlled potential generation of the C_{60} monoanion in dilute solution (ca. 1 mM), using resonance Raman (RR) spectroscopy to provide the needed sensitivity. C_{60} (Texas Fullerenes Corporation) solutions were prepared in 70%/30% toluene/acetonitrile which was 0.1 M in electrochemical grade Bu_4NPF_6 (Fluka) supporting electrolyte. C_{60} monoanions were generated by controlled-potential electrolysis at -1.0 V vs a platinum wire pseudo-reference electrode inside a glovebox in a conventional three-electrode electrochemical cell.⁶ Near-infrared measurements confirmed the electrochemical reduction of C_{60} to the monoanion. The near-infrared spectra of the monoanion were essentially identical to those found in the literature.⁷ All Raman measurements were made using 20-mW 356.4-nm Kr^+ (Coherent Innova, Model I-100) excitation, near the absorption maximum (339 nm) of C_{60}^- in the near UV.⁶ Raman scattered radiation was dispersed using a 1.25-m single spectrograph equipped with

a 3600-groove/mm holographic grating and an intensified diode array detector. All Raman spectra were recorded at 3 cm^{-1} resolution.

RR spectra are compared in Figure 1 for the neutral and monoanion species. The pentagonal pinch mode is strongly enhanced and shifts down by 6 cm^{-1} upon monoanion formation, a value exactly in accord with the doped film data, if electron transfer from potassium to C_{60} is complete.⁸

Since the C_{60} LUMOs are degenerate, the anion is subject to Jahn-Teller (J-T) distortion.⁹ The previously reported SERS spectra contain prominent bands at the positions of non-totally symmetric modes, some of which show evidence of splittings. These effects were suggested to arise from symmetry lowering due to surface interactions and the field gradient, as well as to J-T distortions.³⁻⁵ A non-totally symmetric Hg mode at 1424 cm^{-1} is seen weakly in our neutral C_{60} spectrum, but not in the C_{60}^- spectrum (Figure 1). No band is seen in either spectrum near 1560 cm^{-1} , where a strong SERS band appears.³⁻⁵ We have also examined the $700\text{--}800\text{ cm}^{-1}$ region, where band splittings are reported in the C_{60}^- SERS spectrum,⁴ but have seen no features in the C_{60} or C_{60}^- RR spectra. Although additional data at higher sensitivity are needed to evaluate the issue quantitatively, it is apparent that the J-T effect does not provide significant RR enhancement, at least with 356.4-nm excitation. Instead the RR enhancement is mainly restricted to the totally symmetric pentagonal pinch mode, consistent with Franck-Condon scattering from an allowed excited state which is mainly displaced along the pentagonal pinch coordinate. RR enhancement is weaker for C_{60}^- than for C_{60} , as judged by the relative intensities of the solvent bands, consistent with the broader electronic absorption band observed for the anion.⁶

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Oxygen-Atom Transfer from Nitrous Oxide to a Nickel Metallacycle. Synthesis, Structure, and Reactions of (2,2'-Bipyridine)Ni(OCH₂CH₂CH₂)₂

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Nitrous oxide ($N=N=O$) is one of the most thermodynamically potent oxygen-transfer reagents,¹ comparable in oxidizing power to hydrogen peroxide or perbromate, yet it is kinetically inert toward most organic substrates in the absence of a suitable activating agent. These facts have led us to investigate its use as an oxidant in organometallic systems in which transition-metal centers serve to activate N_2O . Our previous studies have centered on early transition-metal (Ti, Zr, Hf) systems in which the inherent strength of the M-O bonds that are formed place limits on potential applications of the reactions of N_2O that we have discovered (precluding, for example, catalytic cycles that might require reductive elimination involving the M-O linkage).²⁻⁵ We have

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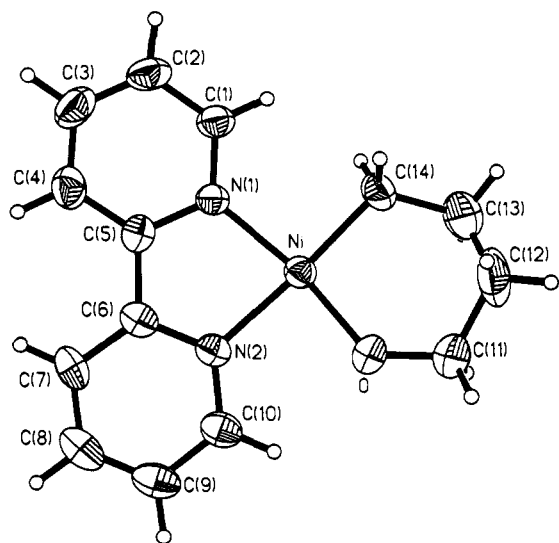
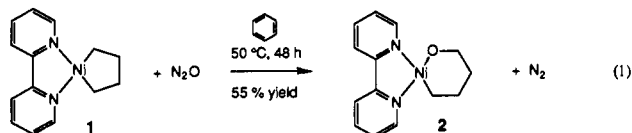


Figure 1. Molecular structure of $2 \cdot 1/2 C_6H_6$. Selected metrical parameters: Ni–O = 1.815(6) Å, Ni–C(14) = 1.921(8) Å, Ni–N(1) = 1.919(6) Å, Ni–N(2) = 1.973(6) Å, N(1)–Ni–C(14) = 94.4(3)°, N(1)–Ni–N(2) = 81.9(3)°, O–Ni–N(1) = 169.1(3)°, O–Ni–N(2) = 88.0(3)°, O–Ni–C(14) = 95.9(3)°, N(2)–Ni–C(14) = 174.9(4)°.

recently turned our attention to studying late-metal systems that do not form such strong bonds with heteroatoms, and herein we report the first example of N_2O oxidation of a metal–carbon bond of a d^8 nickel complex and the structure and reaction chemistry of the resulting oxametallohexane.

Nitrous oxide reacts (1 atm, 50 °C, 48 h) with benzene solutions of the metallacyclopentane complex (bipy)Ni(C_4H_8) (**1**; bipy = 2,2'-bipyridine)⁶ to effect a formal O-atom insertion into a Ni–C bond with elimination of dinitrogen, affording purple (bipy)Ni(OC_4H_8) (**2**) in 55% isolated yield (eq 1),⁷ along with an insoluble



brown precipitate. Heating isolated samples of **2** under N_2O (C_6H_6 , 60 °C, 48 h) results in precipitation of a similar brown product, suggesting that the moderate yield of **2** is limited by its slower secondary reaction with N_2O . 1H and ^{13}C NMR data for **2** indicate the presence of a coordinated bipyridine (all atoms inequivalent) and four inequivalent methylene units,⁷ consistent with the formulation of **2** as a square-planar, d^8 oxametallohexane complex. This was confirmed by an X-ray structural analysis (see Figure 1).⁸ No intermediates are observed in the **1** \rightarrow **2** transformation, although it is reasonable to invoke coor-

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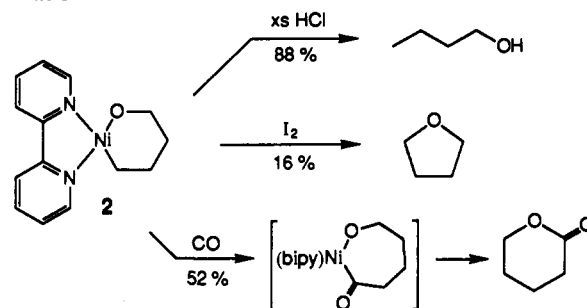
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(7) For **2**: 1H NMR (C_6D_6 , 500 MHz) δ 1.32 (q, CH_2 , 2 H), 2.03 (t, $NiCH_2$, 2 H), 2.10 (q, CH_2 , 2 H), 4.06 (t, OCH_2 , 2 H), 6.25 (t, bipy, 1 H), 6.61 (d, bipy, 1 H), 6.74 (m, bipy, 2 H), 6.83 (t, bipy, 1 H), 6.92 (t, bipy, 1 H), 8.29 (d, bipy, 1 H), 9.77 (d, bipy, 1 H); ^{13}C NMR (C_6D_6 , 75.57 MHz) δ 155.8 (s, bipy), 151.1 (s, bipy), 148.1 (d, bipy), 147.2 (d, bipy), 135.9 (d, bipy), 132.7 (d, bipy), 124.7 (dd, bipy), 124.2 (dt, bipy), 120.7 (dd, bipy), 118.5 (dd, bipy), 65.3 (t, OCH_2), 39.0 (t, CH_2), 26.6 (t, CH_2), 15.5 (t, CH_2).

(8) Crystal data for $C_{14}H_{16}N_2NiO \cdot 1/2 C_6H_6$: monoclinic, $C2/c$, $a = 26.624(5)$ Å, $b = 9.655(2)$ Å, $c = 14.256(3)$ Å, $\beta = 121.85(3)^\circ$, $V = 3112.6(11)$ Å³, $Z = 8$, $D_c = 1.392$ g cm⁻³, $\mu(Mo K\alpha) = 12.50$ cm⁻¹, $T = 296$ K. Of 2406 data collected (purple crystal, $4^\circ \leq 2\theta \leq 47^\circ$), 2297 were independent and 1301 observed ($4\sigma F_o$). The asymmetric unit consists of one molecule of the Ni complex and $1/2$ molecule of benzene, the recrystallization solvent, on a 2-fold rotational axis. With all non-hydrogen atoms anisotropic and all hydrogen atoms assigned idealized locations: $R(F) = 5.30\%$ and $R(wF) = 5.63\%$.

Scheme 1



dination of N_2O to **1** (via a 5-coordinate, TBP intermediate) prior to N_2 loss and oxygen transfer. An azoxy-type intermediate, analogous to those seen in the N_2O oxidations of coordinated alkynes to oxametallacyclobutenes in zirconocene systems,^{4,5} might be involved in this reaction. In contrast to the efficacy of N_2O in the synthesis of **2**, under identical reaction conditions pyridine N -oxide does not react with **1** (C_6H_6 , 50 °C, 48 h), while the action of O_2 on **1** results in elimination of cyclobutane.⁹ The reaction of N_2O (C_6H_6 , 20 °C, 24 h) with the acyclic dialkyl complex (bipy)Ni(CH_2CH_3)₂ (**3**)¹⁰ gives (bipy)Ni(OCH_2CH_3)(CH_2CH_3) (**4**) in 59% yield,¹¹ suggesting that the N_2O oxidation of nickel alkyls to alkoxides might be general, and we are currently investigating this notion.

The Ni–O and Ni–C bonds of **2** can be cleanly protonated by HCl to give 1-butanol, and elimination of tetrahydrofuran from **2** can be effected by the action of I_2 , as shown in Scheme I. Although THF is isolated in only 16% yield from **2**, it suggests that subsequent reaction chemistry of metal–oxygen bonds generated in the reactions of organometallic complexes with N_2O might be richer for the late-transition series metals than for the early transition ones.

Carbon monoxide (1 atm) reacts with **2** to give δ -valerolactone in 52% isolated yield (Scheme I). Infrared spectroscopy indicates that (bipy)Ni(CO)₂ is a coproduct,¹² but it has not been quantified. Ester formation probably proceeds via initial insertion of CO into the Ni–C bond of **2**, followed by reductive elimination to give the lactone. This two-step sequence has precedent in related acyclic Ni(II) and Pd(II) systems: excess CO reacts with (bipy)Ni(Me)(OPh) to give MeCO₂Ph quantitatively, and the acyl intermediate (bipy)Ni{C(O)Me}(O-*p*-C₆H₄-CN) can be intercepted (without reductive elimination of the ester) when (bipy)Ni(Me)(O-*p*-C₆H₄-CN) is treated with a stoichiometric amount of CO.¹³

In summary, the reaction of the nickelacyclopentane **1** with N_2O (eq 1) provides the first example of a clean alkyl \rightarrow alkoxy transformation using nitrous oxide as the oxidant. A similar O-transfer reaction is observed when the diethyl nickel complex **3** is treated with N_2O , affording an ethoxide derivative. The oxanickelacycle **2** undergoes reactions with HCl, I_2 , and CO under mild conditions at both the Ni–C and Ni–O bonds. We are currently investigating the generality of these oxidations since such reactivity could be important in transition-metal-catalyzed oxidations of organics using N_2O .

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(11) For **4**: 1H NMR (C_6D_6 , 300 MHz) δ 1.45 (t, CH_3 , 3 H), 1.63 (q, CH_2 , 2 H), 1.79 (t, CH_3 , 3 H), 4.09 (q, CH_2 , 2 H), 6.29 (t, bipy, 1 H), 6.65–6.92 (m, bipy, 5 H), 8.52 (d, bipy, 1 H), 9.72 (d, bipy, 1 H); ^{13}C NMR (C_6D_6 , 75.57 MHz) δ 155.9, 151.2, 149.1, 148.1, 136.0, 132.7, 125.4, 124.2, 120.8, 118.5, 60.9, 23.0, 15.8, 10.0.

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Supplementary Material Available: Experimental, spectroscopic, analytical, and crystallographic details, atomic coordinates, bond angles and distances, anisotropic thermal parameters, hydrogen atom coordinates (12 pages); observed and calculated structure factors (6 pages). Ordering information is given on any current masthead page.

Mechanism of CO Substitution in the 19-Electron Complex (MeCp)Mn(CO)₂NO

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Organometallic radicals containing 17 or 19 electrons about the metal have been recognized as playing an important role in a variety of transformations.¹ This is due in large part to the greatly increased rate of ligand substitution shown by the radicals when compared to 18-electron analogues. Ligand substitution at 17-electron centers generally follows an associative mechanism.² Very little quantitative information is available concerning ligand substitution at 19-electron centers, although it is often assumed that the mechanism is dissociative.^{3,4} Of the two detailed mechanistic studies of 19-electron complexes reported to date, one showed that the arene in (arene)Fe(Cp) is replaced by phosphines via an *associative* pathway; it is likely, however, that successive arene ring slippage occurs to avoid the formation of 21-electron intermediates.⁵ A second study concerns dissociative CO substitution in Co(CO)₃L₂ (L₂ is 2,3-bis(diphenylphosphino)maleic anhydride).⁶ In this case, however, it is known from recent ESR studies that the molecule is predominantly an 18-electron complex

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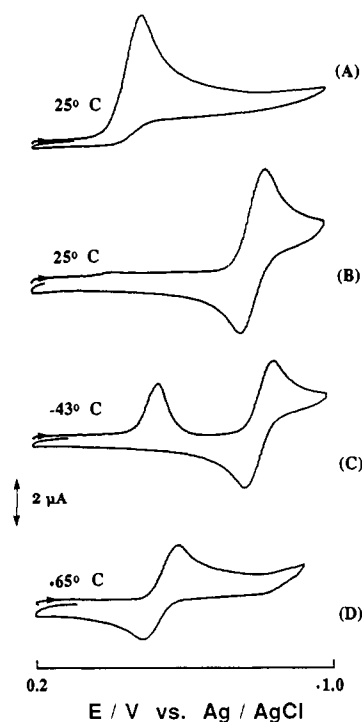
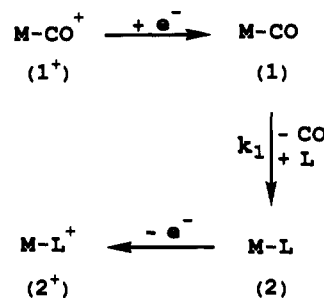


Figure 1. Cyclic voltammograms of 1.0 mM [(MeCp)Mn(CO)₂NO]PF₆ (1⁺) in CH₂Cl₂/0.10 M Bu₄NPF₆ at the indicated temperatures with P(OEt)₃ present at a concentration of (A) 0 mM and (B–D) 10 mM. The working electrode was a 1.0 mm diameter glassy carbon disk, and the scan rate was 0.50 V/s. All potentials are relative to ferrocene E_{1/2} = 0.52 V.

Scheme I



with a radical ligand; only 1.6% of the unpaired spin density is located on the metal.⁷

Herein it is shown that (MeCp)Mn(CO)₂NO⁺ (1⁺) undergoes efficient electron transfer catalyzed (ETC) substitution of CO by a range of P-donors (L = PBu₃, PPh₃, P(OPh)₃, P(OEt)₃, diphos, etc.) and that the initially formed 19-electron complex 1 reacts with L via a strictly dissociative pathway to give (MeCp)Mn(CO)(L)NO (2), which then is spontaneously oxidized to product 2⁺. Cyclic voltammetry of 1⁺ at 25 °C showed that the cathodic current due to the reduction of 1⁺ is completely suppressed in the presence of L and that new reversible couples at more negative potentials appear, which are due to 2⁺/2. A typical CV (with L = P(OEt)₃) is shown in Figure 1B. Proof of the identity of 2⁺ was provided by voltammetry of genuine samples⁸ and by IR spectra obtained after bulk electrolysis of 1⁺ in the presence of 2 equiv of L; complete conversion to 2⁺ occurred after the passage of only 0.03 mol of electrons/mole of 1⁺.

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