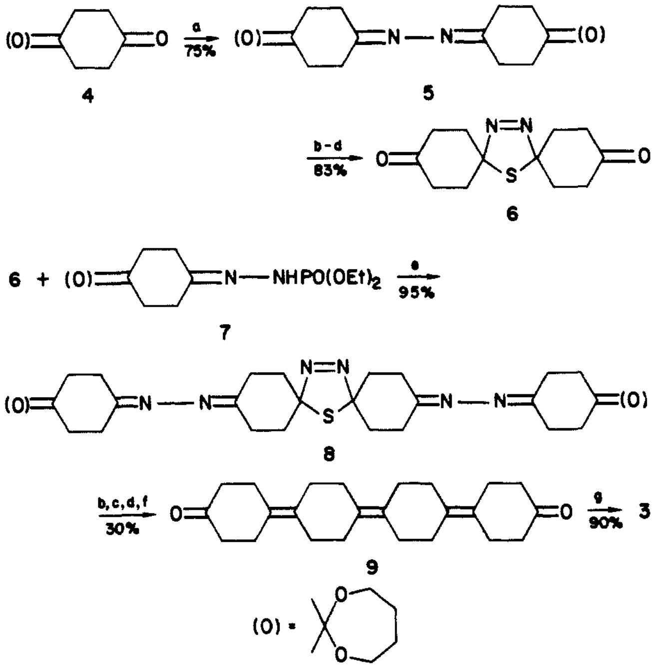
Scheme I.^{a} Synthesis of Pentacyclo[12.2.2.2^{2,5}.2^{6,9}.2^{10,13}]-1,5,9,13-tetracosatetraene



^{a}(a) N_2H_4; EtOH; (b) H_2S, CH_3CN; (c) $Pb(OAc)_4$, CH_2Cl_2; (d) HCl, H_2O, CH_2Cl_2; (e) NaH, THF; (f) toluene, Δ; then $P(OEt)_3$, Δ; (g) $TiCl_3/Zn/Cu$, dimethoxyethane, 48 h addition, Δ.

3, might be particularly interesting because it might be capable of complexing metal ions in its cavity.

Tetraene 3 was prepared as shown in Scheme I. Reaction of hydrazine with the tetramethylene monoacetal of 1,4-cyclohexanedione[3] (4) gave the symmetrical azine 5, which was converted into diketothiadiazoline 6 on treatment with H_2S in acetonitrile followed by oxidation with lead tetraacetate and hydrolysis with aqueous acid. Coupling[4] of 6 with phosphonohydrazide 7 and then gave 8. Addition of H_2S to 8, oxidation with lead tetraacetate, deprotection by treatment with aqueous acid, and heating, first in toluene to effect a 3-fold extrusion of nitrogen and then in triethyl phosphite to remove sulfur, gave diketone 9.[5] Slow addition of diketone 9 over a 48-h period to a refluxing slurry of $TiCl_3/Zn/Cu$ in dimethoxyethane according to our previously published general procedure[6] provided tetraene 3 in 90% yield.[7] Single-crystal X-ray analysis confirmed the structure and indicated a distance of 5.11 Å between double bonds across the ring.

If tetraene 3 is to act as an eight-electron, square-planar ligand for complexation with d^8 or d^{10} metals, stringent criteria must be met. First, the symmetries and energy levels of ligand and metal orbitals must be compatible (this may be a source of difficulty with d^{10} metals, which do not adopt square-planar geometry); second, the size of the ligand's cavity (5.11-Å diameter) requires a metal-to-carbon bond distance of approximately 2.5 Å; third, the metal atom or ion must be stripped of all other ligands, including solvent, before it will be able sterically to enter the cavity.

Of the transition metals that might meet these criteria, Ag(I) was chosen because it is known[8] to form silver–olefin complexes with bond lengths of 2.4–2.6 Å and because its weakly ligated trifluoromethanesulfonate (triflate) salt is readily available. When powdered tetraene 3 was added to a stirred solution of silver triflate in tetrahydrofuran (THF) at room temperature, the normally insoluble olefin dissolved within minutes to form a homogeneous solution from which a new white powder slowly precipitated. Recrystallization of the powder from THF yielded a crystalline silver–olefin complex (66%) that was shown by ^1H and ^{13}C NMR spectra to have a highly symmetrical structure.[9] In addition, the ^{13}C NMR spectrum showed carbon–silver coupling indicative of a static, stable complex. Single-crystal X-ray analysis[10] confirmed the structure of the complex as 10 (Figure 1). Compound 10 proved stable to air, heat, light, and hydroxylic solvents under conditions that instantly destroy normal silver–olefin π complexes. To our knowledge, this is the first example, both of a static silver–olefin complex and of a square-planar d^{10} organometallic complex. We are continuing our work in hope of generating complexes of 3 with other metals.

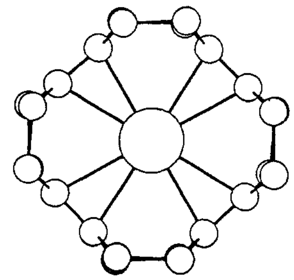


Figure 1. Computer-generated X-ray crystal structure of silver–olefin complex **10**.

Acknowledgment. This work was supported by the donors of the Petroleum Research Fund, administered by the American Chemical Society, and by the National Science Foundation (Grant CHE-8207890).

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[7] Data for triene 3: mp >300 °C; ^1H NMR ($CDCl_3$) AA'BB' δ 1.9–2.2 (m, 16 H), 2.2–2.5 (m, 16 H); ^{13}C NMR ($CDCl_3$) δ 129.56, 27.90.

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[9] Data for complex 10: mp 145 °C dec; ^1H NMR ($CDCl_3$) AA'BB' δ 2.11 (m, 16 H), 2.87 (m, 16 H); ^{13}C NMR ($CDCl_3$) δ 135.15, 135.12, 28.76, 28.74.

[10] Crystals of 10 formed in the monoclinic space group $P2_1/c$ with a = 16.189 (2) Å, b = 9.814 (1) Å, c = 16704 (2) Å, and β = 60.92 (2)°. Block-diagonal least-squares refinements with anisotropic nonhydrogen atoms and isotropic hydrogens converged to a residual of 0.060 for the 2319 observed reflections. Complete structural details will be given in a subsequent publication.

First Insertion of NO into a Transition-Metal Cluster–Carbon Bond: Regioselective Formation, Structure, and Reactions of the First Alkanenitrile Oxide Complexes

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The chemistry of NO in the presence of transition metals is receiving considerable current attention because of its role in air pollution,[1] its potential in organic synthesis by carbon–nitrogen bond formation,[1,2] and an increasing interest in its basic features.[3]

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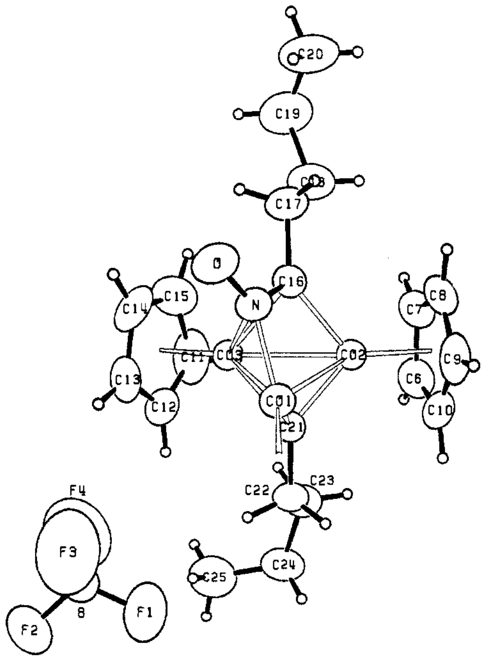
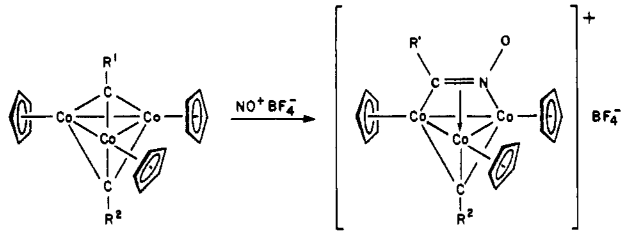


Figure 1. ORTEP drawing of **2a**. Ellipsoids are scaled to represent the 50% probability surface.

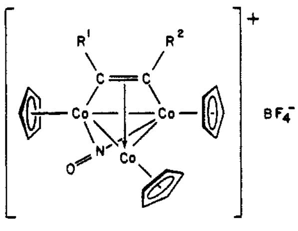
The nitrosyl cation has been reacted with many mono-[4] and polynuclear metal systems,[5] leading mainly to substitution and reduction. Insertion into alkyl and aryl metal bonds in monometallic complexes is documented.[3,6] We report here the unprecedented title reaction and some preliminary chemistry of the products.

While μ_3-η^1-RCCo$_3$(CO)$_9$ undergoes substitution[7] with NO$^+$, the analogous, but chemically quite different,[8] clusters [μ_3-η^1-CR^1][μ^3-η^1-CR^2][CpCo]$_3$ (**1**)[9] (Cp = η^5-C$_5$H$_5$) are smoothly converted (NO$^+$BF$_4^-$, 23 °C, CH$_3$NO$_2$–CH$_2$Cl$_2$) into the corresponding black crystalline adducts **2**[10] in high yield. Following these transformations by ^{1}H NMR even at low temperatures did not allow the detection of any intermediates. The product structures were initially assigned on the basis of microanalytical and spectral data. Thus, CIMS gives parent ions for the cluster portion, strong bands in the IR spectrum between 1300–1400 are assignable to some kind of a briding NO ligand,[6,11] and, although in the ^{1}H NMR spectra the three Cp's maintain chemical-shift equivalency down to −80 °C, the signals for the two substituents R^1 and R^2 are distinct and have been shifted, one set (R^1) to higher, the other (R^2) to lower field from their original positions. Because of the ultimate uncertainty about the structures of **2**, and because of the novelty of their formation, two X-ray crystallographic analyses were performed on **2a**[10] and **2c**[12] confirming the structural assignments. As shown for **2a** in Figure 1, the NO moiety has inserted into one of the metal–carbon bonds, an unpredecented process that, in addition, has furnished the first al-

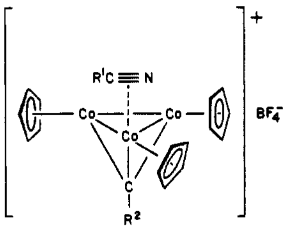


1 **2**

a R^1 = R^2 = CH$_3$CH$_2$CH$_2$CH$_2$, (95%)
b R^1 = CH$_3$CH$_2$CH$_2$CH$_2$; R^2 = H, (83%)
c R^1 = CH$_3$CH$_2$CH$_2$; R^2 = H, (87%)
d R^1 = CH$_3$; R^2 = CO$_2$CH$_3$, (86%)
e R^1 = R^2 = C$_6$H$_5$ (81%)



3a,b



4a,b

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(10) All new compounds gave satisfactory analytical and/or spectral data. For example, **2a**: black plates, mp >250 °C dec; IR (KBr) 3060 (w), 2950 (m), 1690 (w), 1410 (m), 1300 (ms), 1140 (s), 825 (m) cm^{-1}; ^{1}H NMR (250 MHz, acetone-d_6) δ 1.29 (t, J = 7 Hz, 3 H), 1.33 (t, J = 7 Hz, 3 H), 1.95 (m, 2 H), 2.10 (m, 2 H), 3.10 (m, 4 H), 3.90 (t, J = 7 Hz, 2 H), 5.25 (s, 15 H), 5.24 (t, J = 7 Hz, 2 H); ^{13}C{^{1}H} NMR (CDCl$_3$) δ 14.1, 14.6, 23.5, 23.9, 29.9, 38.9, 47.1, 74.9, 90.0, 165.4 (carbyne carbon not located); CIMS (relative intensity) m/e 540 (M$^+$ cation, 18.4), 457 (11.3), 189 (100). X-ray, crystal size 0.12 × 0.22 × 0.38 mm, space group $P2_1/n$, a = 9.7409 (12) Å, b = 19.8516 (12) Å, c = 13.2601 (9) Å, V = 2541.7 (7) Å^3, μ_{calcd} = 19.80 cm^{-1}, d_{calcd} = 1.639 g cm^{-3}, radiation Mo Kα ($\bar{\lambda}$ = 0.71073 Å), scan range 3–45°, reflections collected 3441, unique 2704 with $F^2 > 3\sigma(F^2)$, R = 0.0288, R_w = 0.0393. **2b**: black crystals, mp >120 °C dec; IR (KBr) 3098 (m, br), 2962 (m), 2938 (m), 2865 (w), 1630 (m, br), 1418 (s), 1305 (s), 1100–1000 (vs, br), 842 (s), cm^{-1}; ^{1}H NMR (300 MHz, acetone-d_6) δ 23.09 (s, 1H), 5.27 (s, 15 H), 3.55 (m, 2 H), 2.16 (m, 2 H), 1.67 (m, 2 H), 1.09 (t, J = 7.3 Hz, 3 H). **3b**: black powder; IR (KBr) 3112 (m, br), 2962 (m), 2928 (m), 2863 (w), 1420 (s), 1385 (s), 1000–1150 (vs, br), 831 (s), 632 (m) cm^{-1}; ^{1}H NMR (acetone-d_6) δ 11.73 (s, 1 H), 5.20 (s, 15 H), 3.81 (m, 2 H), 2.32 (m, 2 H), 1.76 (m, 2 H), 1.13 (t, J = 7.4 Hz, 3 H); ^{13}C{^{1}H} NMR (acetone-d_6) δ 176.7, 139.7, 91.6, 50.5, 34.6, 23.8, 14.4; MS (70 eV, relative intensity), m/e 484 (M$^+$ cation, 8.4), 402 (1.7), 370 (3.2) 247 (22), 189 (100), 124 (20). **4b**: black flakes: IR (KBr) 3119 (w), 3060 (w), 2965 (m) 2938 (m), 2872 (w), 1742 (w), 1640 (w, br), 1428 (m), 1420 (m), 1264 (w), 1150–1000 (vs, br), 842 (s) cm^{-1}; ^{1}H NMR (acetone-d_6) δ 22.70 (s, 1 H), 5.19 (s, 15 H), 4.38 (m, 2 H), 2.46 (m, 2 H), 1.86 (m, 2 H), 1.16 (t, J = 7.3 Hz, 3 H); ^{13}C{^{1}H} NMR (acetone-d_6) δ 373.89 (C carbyne), 204.7 (C–N), 87.9, 53.3, 33.7, 23.7, 14.4.

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kanenitrile oxide bound to transition metals.[13] It appears that in **2a** the nitrogen is attached in a σ fashion to Co1, as is C16 to Co2. The bonding to Co3 is best described as a π-type interaction with the CN double bond. The O–N–C_{16}–C_{17} atoms define an approximate plane, Co1 and -2 located closer (0.32 and 0.53 Å, respectively) to it than Co3 (1.57 Å and on the opposite side). The carbyne half of the remaining cluster has been left relatively unchanged. The structure **2a** is reminiscent of that of related (CpM)$_3$alkyne(CO) complexes[14] and $Fe_3(CO)_9(CH_3CN)(H)$.[15] As will be noted from the examples **1b–d** → **2b–d**, the insertion is *completely* regiospecific, apparently seeking out the more electron-rich metal–carbon bond.

A highly unusual transformation ensued when attempts were made to deprotonate either **2a** or **2b** ($CH_3CH_2CH_2CH_2Li$ or $NaOCH_3$). An isomer was formed in either case, **3a** (37%) and **3b** (41%) on the basis of MS (*m/e* for M$^+$ and M$^+$ – alkyne) and elemental analysis. A strong IR peak at 1420 cm^{-1} suggests the presence of a bridging NO ligand,[11] the ^{1}H NMR spectrum of **3a** reveals two *equivalent* butyl groups and that of **3b** an upfield shift of the original carbyne hydrogen (δ 23.13) to 11.73 pm. The Cp's give sharp signals even at -80 °C. The $^{13}C\{^1H\}$ NMR spectra exhibit peaks typical[16] for those of σ,π-coordinated alkynes (**3a** δ 172.9, **3b** δ 176.7, 139.7) and the IR stretch at 1385 cm^{-1} (seen only for **3b**) is that expected for a cationic (CpCo)$_3$alkyne.[17] On the basis of these data we assign the structure **3** shown for these molecules, the third example[8a,b] of carbyne–carbyne coupling in **1**, occurring under exceedingly mild conditions and involving simultaneous NO deinsertion.

It is interesting to note that both the C–N (1.362 Å) as well as the N–O bond length in **2a** (1.280 Å) are *identical* with the analogous bonds in pyridine *N*-oxide.[18] Since the latter is readily deoxygenated,[19] it became of interest to determine the potential of **2** in oxidation reactions. Indeed, when exposed to CO (10 atm) both **2a** and **2b** converted to two new compounds **4a** (38%) and **4b** (50%), respectively,[10] to which, on the basis of spectral data, we assign the structures of their nitrile analogues μ_3-η^1-CR^2-(CpCo)$_3$(R^{1}CN)$^+$BF$_4^-$. Significantly, the IR spectra reveal the absence of NO and CO absorptions (but strong signals for BF$_4^-$, 1000–1150 cm^{-1})[20] and the ^{1}H and ^{13}C NMR spectra show that reaction must have occurred at the side of the nitrile oxide ligand. For example, the carbyne hydrogen in **4b** resonates at 22.70 ppm, the corresponding carbon at 373.9 ppm. A ^{13}C peak at 204.7 is assigned to the nitrile carbon. Because suitable crystals for X-ray could not be grown, we are not sure about the exact mode of coordination of the R^{1}CN group, but it is very likely similar to the iron system studied by Kaesz et al.[15] Finally, preliminary results show that both **2a** and **3a** react with H_2 (or D_2, 10 atm) in the presence of catalytic Pd (10% on C) to give new difficult to characterize salts, with spectral data suggesting hydrogenolysis of the N–O bond [from **2a**: IR ν_{N-H} 3279 cm^{-1}, ν_{N-D} 2438 cm^{-1}, ν_{BF_4} 1000–1150 (vs, br) cm^{-1}]. A precise structural analysis will have to await the outcome of experiments employing more readily crystallizable systems.

There is considerable current effort to understand the heterogeneously catayzed reduction of NO by H_2 and/or CO,[21] which, under some condition, furnishes C–H bonded products. This observation, in conjunction with the implication of surface carbynes in Fischer–Tropsch catalysis,[22] suggests potential relevance of the chemistry reported here to heterogeneously catalyzed processes.

Acknowledgment. This work was supported by the NSF-CHE 8504987. The crystal structure analyses were carried out by Dr. F. J. Hollander, staff crystallographer on the U.C. Berkeley, Department of Chemistry, X-ray facility (CHEXRAY). K.P.C.V. is a Miller Professor in residence, M.W. was the recipient of a Deutscher Akademischer Austauschdienst Postdoctoral Fellowship (1984–1985).

Supplementary Material Available: Complete spectral data on compounds **2c–e**, **3a**, and **4a**, elemental analyses on the new compounds **1b–d**, **2a–e**, and **3a,b**, a listing of positional and thermal parameters and tables of bond lengths and angles of **2a,b**, and an ORTEP drawing of **2b** (17 pages). Ordering information is given on any current masthead page.

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Rhodium–Rhodium Stretching Frequencies in ^{16}O, ^{18}O, and CD$_3$ Derivatives of $Rh_2(O_2CCH_3)_4(PPh_3)_2$

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The assignment of rhodium–rhodium stretching frequencies, ν(RhRh), in dirhodium tetracarboxylate complexes has long been controversial. The initial indications of San Filippo and Sniadoch,[2] subsequently supported by Kharitonov et al.[3] and Kireeva et al.,[4] were in favor of the range 150–170 cm^{-1} for ν(RhRh) in a variety of complexes of the type $Rh_2(O_2CR)_4L_2$ (L = axial ligand). On the other hand Ketteringham and Oldham,[5] who also studied a range of complexes of this sort, favored the range 288–351 cm^{-1} for ν(RhRh). Recent Raman and extensive electronic spectral analyses by Miskowski et al.[6] on $Rh_2(O_2CCH_3)_4(H_2O)_2$ and $Li_2Rh_2(O_2CCH_3)_4Cl_2{\cdot}8H_2O$ were based on the lower value for ν(RhRh). Since in our view there was no firm evidence one way or the other regarding the correct wavenumber region of ν(RhRh) in dirhodium tetracarboxylate complexes, we undertook detailed electronic, infrared, Raman, and resonance Raman studies of $Rh_2(O_2CCH_3)_4(PPh_3)_2$, as its ^{16}O, ^{18}O, and CD$_3$ variants, in order to resolve this problem definitively in one case at least. The choice of triphenylphosphine as axial ligand is advantageous for resonance

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