

Conversion of $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{PPh}_3)_2$ and Nitro Compounds to Mononuclear $\eta^1(N)$ -Nitrosoalkyl and Dinuclear $\mu\text{-}\eta^1(N):\eta^2(N,O)$ -Nitrosoaryl Complexes

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Received August 2, 2003

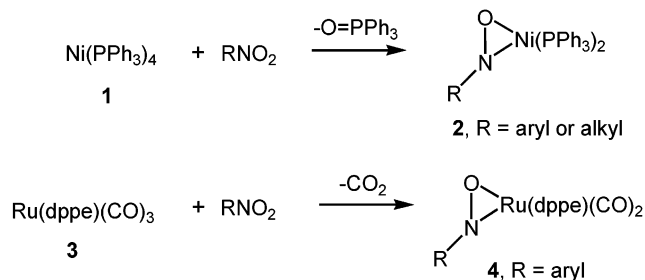
The room-temperature reaction of $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{PPh}_3)_2$ (**5**) with aliphatic nitro compounds, RNO_2 , where $\text{R} = \text{Me}, \text{Et}, i\text{Pr}$, leads to formation of the corresponding $\eta^1(N)$ -nitroso derivatives $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{PPh}_3)[\eta^1(N)\text{-N}(\text{O})\text{R}]$ (**6-Me**, $\text{R} = \text{Me}$; **6-Et**, $\text{R} = \text{Et}$; **6-Pr**, $\text{R} = i\text{Pr}$). Aromatic nitro compounds, ArNO_2 , where $\text{Ar} = -\text{C}_6\text{H}_5, -p\text{-C}_6\text{H}_4\text{C}\equiv\text{CTMS}$, undergo reaction with **5** to give the $\mu\text{-}\eta^1:\eta^2$ -nitroso derivatives, $[(\eta^5\text{-C}_5\text{H}_5)\text{Co}]_2[\mu\text{-}\eta^1(N):\eta^2(N,O)\text{-N}(\text{O})\text{R}]_2$ (**7-Ph**, $\text{R} = -\text{C}_6\text{H}_5$; **7-Ar**, $\text{R} = -p\text{-C}_6\text{H}_4\text{C}\equiv\text{CTMS}$). Complexes **6-Me** and **7-Ar** were characterized by X-ray crystallographic analyses.

Introduction

Nitroso-alkyl and -aryl complexes are of interest as intermediates in the metal-catalyzed carbonylation of nitroaromatics, as inhibitors of cytochrome catalytic function, and as models for metal-dioxygen complexes.¹ Among the useful synthetic routes toward metal-nitroso complexes is the deoxygenation of organic nitro compounds by metal-carbonyl and metal-phosphine complexes.^{2–5} In previous reactions of this type, the mononuclear metal-nitroso products contain a side-bound $\eta^2(N,O)$ -nitroso ligand. For example, Berman and Kochi reported the reaction of $\text{Ni}(\text{PPh}_3)_4$ (**1**) with 2-nitro-2-methylpropane to give the $\eta^2(N,O)$ -nitroso complex **2** and triphenylphosphine oxide (Scheme 1).² In a similar fashion, the carbonyl complex $\text{Ru}(\text{dppe})(\text{CO})_3$ (**3**) undergoes reaction with nitrobenzene to give the $\eta^2(N,O)$ -nitroso complex **4** and carbon dioxide.³ Detailed mechanistic studies, by Kochi² and by Gladfelter,³ indicated that both reactions proceed via an oxygen atom transfer induced by a prior electron transfer from the metal to the nitro substrate.

Herein we report that nitroalkanes undergo reaction with $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{PPh}_3)_2$ (**5**) to give the known⁴ $\eta^1(N)$ -nitroso derivatives $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{PPh}_3)[\eta^1(N)\text{-N}(\text{O})\text{R}]$ (**6-Me**, $\text{R} = \text{Me}$; **6-Et**, $\text{R} = \text{Et}$; **6-Pr**, $\text{R} = i\text{Pr}$). In contrast,

Scheme 1



nitroaryls undergo reaction with **5** to give the dinuclear $\mu\text{-}\eta^1:\eta^2$ -nitroso derivatives $[(\eta^5\text{-C}_5\text{H}_5)\text{Co}]_2[\mu\text{-}\eta^1(N):\eta^2(N,O)\text{-N}(\text{O})\text{R}]_2$ (**7-Ph**, $\text{R} = -\text{C}_6\text{H}_5$; **7-Ar**, $\text{R} = -p\text{-C}_6\text{H}_4\text{C}\equiv\text{CTMS}$). To our knowledge, this is the first example in which a metal complex undergoes reaction with a nitro compound to give an $\eta^1(N)$ -nitroso complex,^{5,6} and the first observation wherein the nature of the nitro organic group (alkyl or aryl) determines the binding mode ($\eta^1(N)$ or $\mu\text{-}\eta^1(N):\eta^2(N,O)$) in products formed from the same starting complex.

Results and Discussion

When nitromethane (0.074 mmol) is added to a benzene-*d*₆ solution (0.32 mL) of the cobalt bis(phosphine) complex⁷ **5** (0.018 mmol), the $\eta^1(N)$ -nitrosomethane complex **6-Me** is formed within 90 min at room temperature (Scheme 2). Integration of the ¹H NMR resonances for **6-Me** at δ 4.42 (s, 5H, C₅H₅) and 2.58 (d, *J*_{PH} = 2.5 Hz, 3H, CoNOCH₃), relative to the methyl hydrogen resonance of the toluene internal standard, indicated a 56% yield of **6-Me**. An infrared spectrum (NaCl) of the crude reaction mixture exhibited a band attributed to the $\nu(\text{NO})$ stretch at 1301 (s) cm⁻¹ and strong bands

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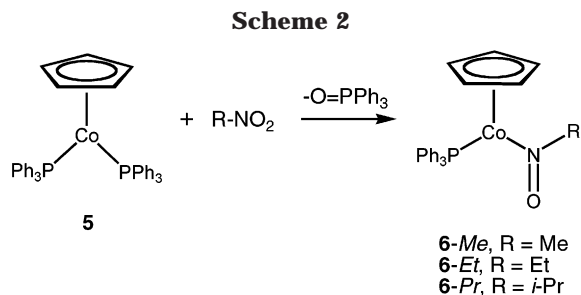
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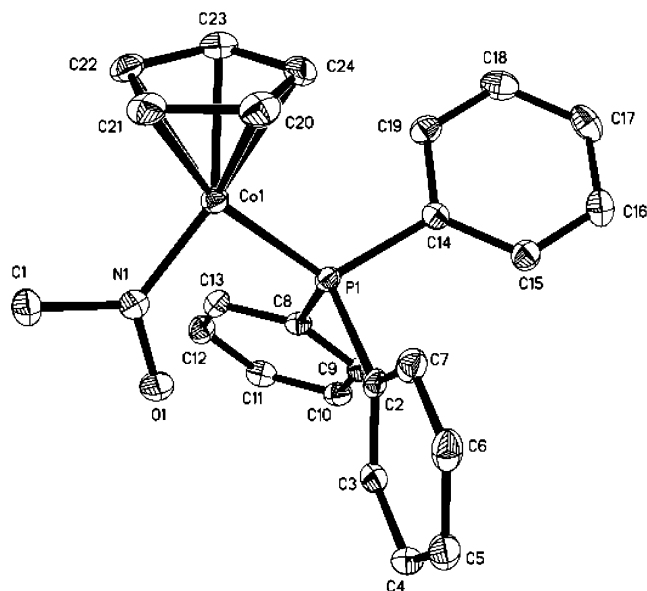
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**Table 1. Crystal Data and Structure Refinement for 6-Me and 7-Ar**

	6-Me	7-Ar
mol formula	C ₂₄ H ₂₃ CoNOP	C ₃₂ H ₃₆ Co ₂ N ₂ O ₂ Si ₂
mol wt	431.33	654.67
cryst syst	triclinic	monoclinic
space group	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>c</i>
temp, K	100(2)	100(2)
<i>a</i> , Å	10.0499(5)	14.722(4)
<i>b</i> , Å	10.8886(6)	8.600(3)
<i>c</i> , Å	20.1659(11)	12.232(4)
α , deg	80.6070(10)	90
β , deg	82.4910(10)	92.035(4)
γ , deg	66.8450(10)	90
<i>V</i> , Å ³	1996.39(18)	1547.6(8)
<i>Z</i>	4	2
<i>D</i> _{calcd} , Mg/m ³	1.435	1.405
abs coeff, mm ⁻¹	0.954	1.180
cryst size, mm ³	0.25 × 0.25 × 0.10	0.38 × 0.13 × 0.09
wavelength, Å	0.710 73	0.710 73
no. of rflns collected	12561	4007
no. of indep rflns	8757 (<i>R</i> (int) = 0.0159)	4007 (<i>R</i> (int) = 0.0000)
refinement method	full-matrix least squares on <i>F</i> ²	
no. of data/params	8757/553	4007/203
goodness of fit on <i>F</i> ²	0.978	1.016
final <i>R</i> indices	<i>R</i> 1 = 0.0324, w <i>R</i> 2 = 0.0814	<i>R</i> 1 = 0.0525, w <i>R</i> 2 = 0.1313
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0391, w <i>R</i> 2 = 0.0835	<i>R</i> 1 = 0.0631, w <i>R</i> 2 = 0.1358
largest diff peak and hole, e Å ⁻³	0.530 and -0.233	1.603 and -0.640

attributed to triphenylphosphine oxide at 1196 and 1118 cm⁻¹. The NO stretch in the IR spectrum of CH₃NO (**8**) is observed at 263 cm⁻¹ higher wavenumber (1564 cm⁻¹, gas-phase value)⁸ than that observed for **6-Me**. The *E* dimer, [CH₃N(O)=N(O)CH₃] (**9**), which has significant NO single-bond character, exhibits $\nu(\text{NO})$ at 1282 cm⁻¹.⁹ The related reactions of **5** (0.063 M) with either nitroethane (3 equiv) or 2-nitropropane (3 equiv) lead to formation of the known η^1 -nitroso complexes **6-Et** (53% yield) and **6-Pr** (38% yield), respectively. In addition to a lower yield, the 2-nitropropane reaction takes 43 h longer to reach completion than does reaction of **5** with either nitromethane or nitroethane.

An X-ray crystallographic analysis of **6-Me** permits a comparison of bond distance and angle data with those determined for both CH₃NO (**8**)¹⁰ and the *E* dimer [CH₃N(O)=N(O)CH₃] (**9**)¹¹ (Figure 1, Tables 1 and 2). For **6-Me**, the N(1)–O(1) distance of 1.2845(19) Å is 0.07 Å longer than the N–O distance in nitrosomethane (1.211 Å) and slightly longer than the 1.25(2) Å N–O

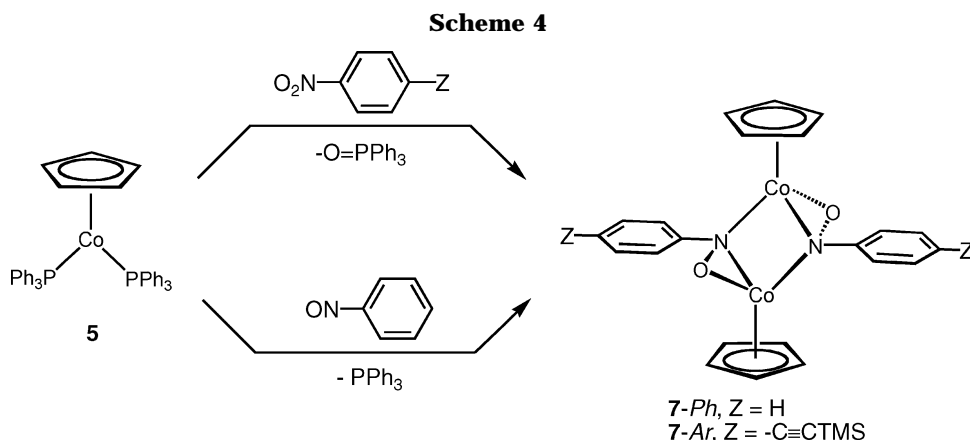
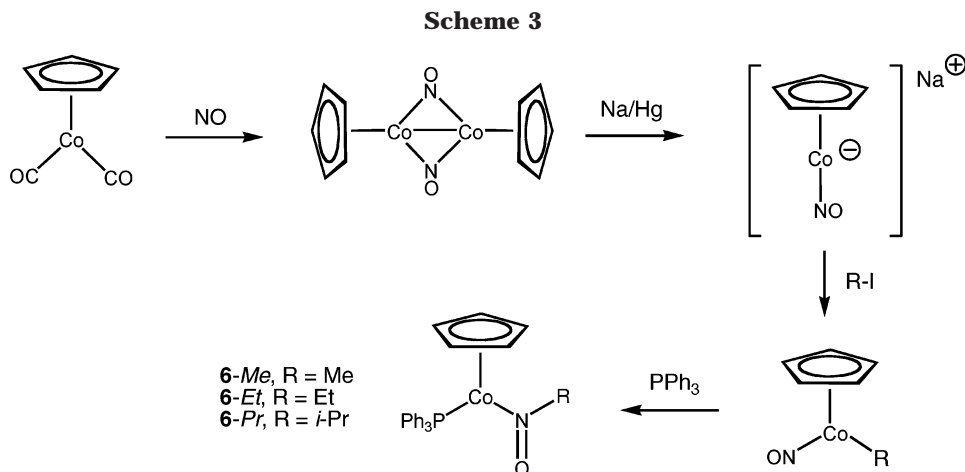
**Figure 1.** ORTEP view of the η^1 -nitroso complex **6-Me** with the atom-numbering scheme (50% probability thermal ellipsoids). Hydrogen atoms are omitted for clarity.**Table 2. Selected Bond Lengths and Angles for 6-Me**

Bond Lengths (Å)							
A	B	dist	A	B	dist		
Co(1)	N(1)	1.7822(16)	P(1)	C(14)	1.8409(18)		
Co(1)	P(1)	2.1835(5)	Co(1)	C(24)	2.0963(19)		
Co(1)	C(20)	2.1099(19)	N(1)	O(1)	1.2846(19)		
Co(1)	C(21)	2.0901(18)	N(1)	C(1)	1.480(2)		
Co(1)	C(22)	2.1006(18)	P(1)	C(2)	1.8359(17)		
Co(1)	C(23)	2.1148(19)	P(1)	C(8)	1.8354(18)		
Bond Angles (deg)							
A	B	C	angle	A	B	C	angle
N(1)	Co(1)	P(1)	90.92(5)	Co(1)	P(1)	C(2)	109.06(6)
Co(1)	N(1)	O(1)	126.33(12)	Co(1)	P(1)	C(8)	119.23(6)
Co(1)	N(1)	C(1)	123.46(13)	Co(1)	P(1)	C(14)	118.57(6)

distance in **9**. This lengthening of the N–O bond relative to the free nitroso compounds is a reflection of significant back-bonding from cobalt(I) to the π^* orbital of the nitroso ligand.^{1a} The geometry about nitrogen is trigonal planar, as determined by only slight deviations of the Co (+0.004 Å), C (+0.004 Å), O (+0.004 Å), and N (–0.012 Å) atoms from the mean plane defined by those atoms. The C(1)–N(1)–O(1) angle of 110.18(15)° in **6-Me** is 3° smaller than in nitrosomethane and ca. 15° less than in **9**. DFT-B3LYP calculations by Niu and Hall on (η^5 -C₅H₅)Co(PH₃)[η^1 (N)–N(O)Me] produced the same 110° C–N–O angle;¹² thus, the relatively small 110° angle in **6-Me** does not appear to be due to steric congestion between the nitroso ligand and the PPh₃ ligand.

The spectroscopic and structural properties of the nitroso complexes were similar to those previously reported by Bergman for the same complexes prepared from (η^5 -C₅H₅)Co(CO)₂, by the route shown in Scheme 3.⁴ The key steps are alkylation of Na[(η^5 -C₅H₅)Co(NO)], migratory insertion of the alkyl ligand into the cobalt–

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nitrosyl bond, and trapping of the unsaturated cobalt–nitroso intermediate by added triphenylphosphine. The yields based on $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{CO})_2$ ranged from 9 to 32% for the four-step sequence.

In addition to being a relatively lengthy route toward complexes **6**, the alkyl halide route shown in Scheme 3 is presumably not applicable to the synthesis of nitrosoaryl complexes from aryl halides. The reaction of **5** with nitroaryls should in principle provide a convenient route toward nitrosoaryl analogues of **6**. Despite the employment of reaction conditions and concentrations similar to those utilized for the synthesis of **6**, the room-temperature reaction of **5** (0.031 mmol) with nitrosobenzene (0.092 mmol) led to formation of the dinuclear $\mu\text{-}\eta^1\text{:}\eta^2$ -nitroso complex $[(\eta^5\text{-C}_5\text{H}_5)\text{Co}]_2[\mu\text{-}\eta^1(N)\text{:}\eta^2(N,O)\text{-N}(\text{O})\text{C}_6\text{H}_5]_2$ (**7-Ph**, Scheme 4) in 21% yield. It was readily apparent from the high-field ^1H NMR (benzene- d_6) chemical shift of the cyclopentadienyl hydrogen resonance at δ 4.04 that **7-Ph** was not a simple analogue of **6**, for which the average cyclopentadienyl hydrogen resonance was observed at δ 4.43. The dimer nature of the complex was revealed from the mass spectrometry analysis, and a literature search revealed that **7-Ph** had been previously prepared from nitrosobenzene and $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\eta^2\text{-CH}_2\text{=CH}_2)_2$ by Floriani.¹³ A more convenient starting material than the bis(ethylene) complex is the bis(phosphine) **5**, which we have determined to also undergo reaction with nitrosobenzene over the course of 90 min at room temperature in

benzene- d_6 to give **7-Ph** in 85% yield. Although **7-Ph** was not previously characterized by NMR spectroscopy, it was structurally characterized.¹³ In addition to the relatively high field C_5H_5 hydrogen chemical shift in the ^1H NMR spectrum of **7-Ph**, the phenyl carbon resonances are observed at 164.5 (ipso), 129.0, 124.6, and 122.3 ppm in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (C_6D_6). These values are very similar to those for nitrosobenzene (166.1, 135.5, 129.4, and 120.9 ppm).¹⁴

An interesting test of chemoselectivity in the nitro to nitroso conversion is found in the reaction of **5** with 1-(4-nitrophenyl)-2-(trimethylsilyl)acetylene. Alkynes are known to undergo facile reaction with **5** to give high yields of cobalt–alkyne complexes, $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\eta^2\text{-R}^1\text{C}\equiv\text{CR}^2)(\text{PPh}_3)$, as well as cobaltacyclopentadienes and arenes derived therefrom.¹⁵ In this work, 1-(4-nitrophenyl)-2-(trimethylsilyl)acetylene (0.013 mmol, 0.039 M) underwent reaction with **5** (0.010 mmol) in benzene- d_6 at room temperature (24 h) to give the dimer $[(\eta^5\text{-C}_5\text{H}_5)\text{Co}]_2[\mu\text{-}\eta^1(N)\text{:}\eta^2(N,O)\text{-(TMSC}\equiv\text{C)C}_6\text{H}_4(\text{NO})]_2$ (**7-Ar**) in 34% yield.

An X-ray crystallographic analysis of **7-Ar** confirmed the centrosymmetric μ -nitroso formulation, with non-bonded Co–Co and Co(1)–O(1A) distances of 2.9908(9) and 2.715 Å, respectively (Figures 2 and 3, Tables 1 and 3). The Co(1)–N(1) distance of 1.920(2) Å in **7-Ar** is slightly shorter than the Co(1)–N(1A) distance of 1.938-

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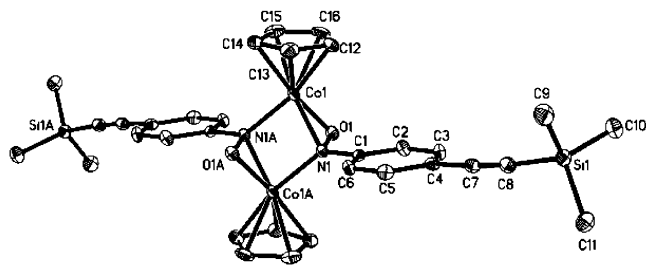


Figure 2. ORTEP view of the $\mu\text{-}\eta^1(\text{N}):\eta^2(\text{N},\text{O})$ -nitroso complex **7-Ar**, with the atom-numbering scheme (50% probability thermal ellipsoids). Hydrogen atoms are omitted for clarity.

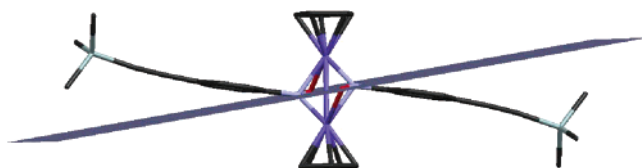


Figure 3. Side view of **7-Ar** showing deviations of atoms from the O(1)–N(1)–O(1A)–N(1A) plane.

Table 3. Selected Bond Lengths and Angles for 7-Ar

Bond Lengths (Å)							
A	B	dist	A	B	dist		
Co(1)	O(1)	1.9032(19)	Co(1)	C(16)	2.073(3)		
Co(1)	N(1)	1.920(2)	N(1)	O(1)	1.374(3)		
Co(1)	N(1A)	1.938(2)	N(1)	C(1)	1.411(3)		
Co(1)	C(12)	2.066(3)	C(4)	C(7)	1.437(4)		
Co(1)	C(13)	2.072(3)	C(7)	C(8)	1.203(4)		
Co(1)	C(14)	2.044(3)	C(8)	Si(1)	1.848(3)		
Co(1)	C(15)	2.078(3)					
Bond Angles (deg)							
A	B	C	angle	A	B	C	angle
O(1)	Co(1)	N(1)	42.13(8)	O(1)	N(1)	Co(1A)	108.92(15)
O(1)	Co(1)	N(1A)	91.73(9)	C(1)	N(1)	Co(1A)	127.52(18)
N(1)	Co(1)	N(1A)	78.34(10)	Co(1)	N(1)	Co(1A)	101.66(10)
N(1)	O(1)	Co(1)	69.58(12)	C(2)	C(1)	N(1)	123.3(2)
O(1)	N(1)	C(1)	115.4(2)	C(6)	C(1)	N(1)	116.9(2)
O(1)	N(1)	Co(1)	68.29(13)	C(4)	C(7)	C(8)	177.0(3)
C(1)	N(1)	Co(1)	119.58(17)	C(7)	C(8)	Si(1)	175.0(3)

(2) Å, and both Co–N distances are much longer than the 1.7822(16) Å Co–N distance observed in the η^1 -nitroso complex **6-Me**. The N(1)–O(1) distance of 1.374(3) Å in **7-Ar** is also significantly longer than the 1.2845(19) Å N–O distance in **6-Me** and is consistent with a Co(III) formal oxidation state in **7-Ar**. The η^2 -nitroso group exhibits a Co(1)–N(1)–O(1) angle of 64.29(13)° in **7-Ar** which compares with the η^1 -nitroso Co–N–O angle in **6-Me** of 126.33(12)° and the Co(1A)–N(1)–C(1) angle of 127.52(18)° in **7-Ar**. The O(1)–N(1)–O(1A)–N(1A) plane bisects the plane of the cyclopentadienyl ligands at an angle of 8.1°, and the mean plane of the phenyl ring bisects the O(1)–N(1)–O(1A)–N(1A) plane by 17.3° (Figure 3). The C(4)–C(7)–C(8) angle and C(7)–C(8)–Si angle are 177.0(3) and 175.0(3)°, respectively, and there is a pronounced bending of the alkyne *sp* carbons and the silicon atom away from the O(1)–N(1)–O(1A)–N(1A) plane. The deviations C(7), C(8), and Si(1) from that plane are 1.72, 2.19, and 3.06 Å, respectively. The bending at C(7) and C(8) is attributed to the well-established ease of bending about *sp*-hybridized carbon centers¹⁶ and crystal lattice packing forces

that appear to stem from nonbonding interactions between the trimethylsilyl groups on neighboring dimers within the lattice (Figure 4, in the Supporting Information).

While the modest yields for the formation of **6** and **7** preclude mechanistic studies, it is reasonable that the reaction mechanism may involve an oxygen atom transfer induced by a prior electron-transfer process, as was established by Kochi² and by Gladfelter³ for the formation of complexes **2** and **4** (Scheme 1). Scheme 5 depicts a possible mechanism for the **5** to **6** conversion, by analogy to the Kochi mechanism for the conversion of **1** to **2**. Loss of triphenylphosphine from **5** to give $[(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{PPh}_3)]$ (**10**) is well established for substitution reactions of **5**.^{17,18} Single-electron transfer (possibly inner-sphere) from **10** to RNO₂ leads to the ion pair **11**, involving a cobalt radical cation and nitro radical anion. Kochi has demonstrated that nitroaryl radical anions generated by electrochemical techniques in the presence of phosphine do not give phosphine oxide.² Collapse of the ion pair **11** would give intermediate **12**, followed by cyclization to **13**. Subsequent fragmentation of **13** to triphenylphosphine oxide and trapping of the resultant η^2 -nitroso intermediate **14** with triphenylphosphine would then give the nitroso species **6**. Computational studies by Niu and Hall indicate that intermediate **14** (R = Me) would have a weak Co–O interaction,¹² with a 2.09 Å Co–O distance and a Co–N–C angle of 156.8°. The calculations further indicated that **14** (R = Me) associates phosphine to give the PH₃ analogue of **6** with essentially no barrier.¹⁹ Alternative mechanisms would include one involving an outer-sphere single electron transfer from **5** to RNO₂, followed by recombination to 18-electron bis(phosphine) analogues of **12** and **13**, with loss of OPPH₃ from **13** directly giving **6**. A mechanism of this type is disfavored by our observation that the rate of reaction for **5** and nitromethane is retarded by added triphenylphosphine.²⁰

In principle, intermediate **14** could lead to both mononuclear η^1 -nitroso products **6** and dinuclear $\mu\text{-}\eta^1$: η^2 -nitroso products **7**. Floriani speculated that the structural features of **7-Ph** suggest that its formation from $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\eta^2\text{-CH}_2=\text{CH}_2)_2$ and nitrosobenzene may actually occur via reaction of the nitrosobenzene dimer with cobalt.¹³ If a mechanism similar to that shown in Scheme 5 is operative, then the nitrosoaryl

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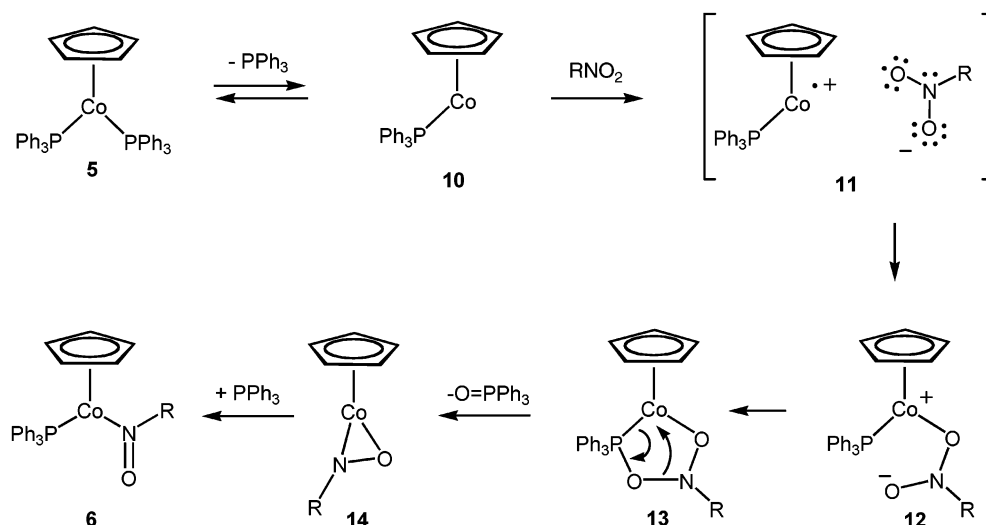
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(19) Although calculations indicate that **14** readily associates PH₃ to give an analogue of **6**, the calculations also indicate that **14** is probably not an intermediate in the NO insertion shown in Scheme 3 (see Figure 3 in ref 12a).

(20) It proved difficult to monitor the reaction of **5** with nitromethane by ¹H NMR spectroscopy due to severe line broadening in the ¹H NMR spectrum. However, after 90 min at room temperature, the signals became sharp and it was possible to establish a 56% yield by integration relative to toluene as internal standard (see the Experimental Section). A ¹H NMR spectrum of a benzene-*d*₆ (0.68 mL) solution of **5** (11.9 mg, 0.018 mmol, 0.027 M), triphenylphosphine (48.4 mg, 0.184 mmol, 0.272 M), nitromethane (3.0 μ L, 0.055 mmol), and toluene (internal standard) exhibited sharp resonances and essentially no reaction after 90 min. After 7 h a ¹H NMR spectrum indicated an 11% yield of **6-Me** and after 24 h only a 28% yield.

Scheme 5



Scheme 6



ligand would be generated within the coordination sphere of cobalt and therefore would be unlikely to involve in situ formation of a nitroso dimer. On the basis of the barrierless association of PH_3 to **14**, it is unlikely that **14** would undergo dimerization to give **7** at a rate competitive with trapping by triphenylphosphine. The preference for η^1 binding with nitrosoalkyls and $\mu\text{-}\eta^1\text{:}\eta^2$ binding for nitrosoaryls may be due to the better π -acceptor ability of the nitrosoaryl ligands relative to the nitrosoalkyl ligands. Computational studies indicate that the $\eta^2(N,O)$ -nitroso complex $(\text{PH}_3)_2\text{Pt}[\eta^2(N,O)\text{-N(O)-CF}_3]$ is more stable than $(\text{PH}_3)_2\text{Pt}[\eta^2(N,O)\text{-N(O)CH}_3]$, consistent with the better π -acceptor ability of CF_3NO .²¹ The observation that $(\text{PMe}_3)_2\text{Co}(\text{Me})(\text{NO})$ undergoes rearrangement to the $\mu\text{-}\eta^1\text{:}\eta^2$ -nitrosomethane complex **15**²² provides an interesting counterpoint to the formation of the cobalt-nitrosomethane compound **6-Me** (Scheme 6). The differing binding modes for nitrosomethane in **6** and **15** may be the result of a more electron-rich metal center in **15**, which would favor a cobalt(III) product.

Conclusions

Ligand substitution by nitrosoalkanes provides the most direct route to $\eta^1(N)$ -nitrosoalkane complexes; however, this approach has been primarily limited to nitroso compounds with bulky alkyl groups ($t\text{BuNO}$ and $i\text{PrNO}$), due in part to the favorable formation of nitroso dimers and tautomers in the less bulky nitroso compounds.^{5,23} A promising route toward less sterically encumbered nitrosoalkyl complexes is the reduction of

readily available nitroalkanes by metal-phosphine complexes. This report represents a second example of such a nitroalkane to metal-nitrosoalkane transformation and the first reduction of nitroalkanes by an organometallic complex to give $\eta^1(N)$ -nitrosoalkane products. Although the yields are modest, this synthetic route is currently the most direct approach to the cobalt η^1 -nitrosoalkanes described herein. In addition, the reactions of $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{PPh}_3)_2$ (**5**) with nitro compounds are unusual in that nitroalkanes give mononuclear $\eta^1(N)$ -nitroso products, whereas nitroaryls give $\mu\text{-}\eta^1(N)\text{:}\eta^2(N,O)$ -nitroso products.

Experimental Section

$(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{PPh}_3)[\eta^1(N)\text{-N(O)Me}$ (6-Me**).** Under a nitrogen atmosphere, nitromethane (4.0 μL , 0.074 mmol) was syringed into an NMR tube containing a benzene- d_6 (0.32 mL) solution of $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{PPh}_3)_2$ (**5**; 11.7 mg, 0.018 mmol, 0.056 M) and toluene (internal standard). The tube was sealed under a nitrogen atmosphere and maintained at room temperature for 90 min, at which time a ^1H NMR spectrum of the sample indicated a 56% yield of **6-Me**.

In a preparative-scale experiment, nitromethane (245 μL , 4.52 mmol) was syringed into a benzene solution (15 mL) of **5** (0.980 g, 1.51 mmol) under a nitrogen atmosphere. After the mixture was stirred at room temperature for 20 h, a portion of the sample was removed and examined by IR spectroscopy (see below). The solvent was removed from the remainder of the sample and the residue washed with hexanes (3 mL). The crude product was then dissolved in benzene (~ 0.25 mL), and hexanes (~ 1.5 mL) were added to precipitate a mixture of triphenylphosphine oxide (TPPO) and black crystals of **6-Me**. Several X-ray-quality crystals of **6-Me** were selected, and a crystal structure determination was carried out. Data for **6-Me** are as follows. IR (neat, NaCl; crude mixture containing **6-Me** and TPPO): 1589 (w, TPPO), 1481, 1436, 1301, 1195 (s, TPPO), 1118 (s, TPPO) cm^{-1} . ^1H NMR (C_6D_6): δ 2.58 (d, 3H, $J_{\text{PH}} = 2.5$ Hz, CH_3), 4.42 (s, 5H, C_5H_5), 7.05 (m, 9H, C_6H_5), 7.75 (m, 6H, C_6H_5). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): δ 66.1, 81.4, 129.4, 134.4 (d, $J_{\text{PC}} = 11.4$ Hz), 135.7, 160.5.

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($\eta^5\text{-C}_5\text{H}_5\text{Co}(\text{PPh}_3)[\eta^1(\text{N})\text{-N}(\text{O})\text{Et}]$ (**6-Et**). In a fashion similar to the reaction above, a dry benzene- d_6 (0.46 mL) solution of **5** (18.6 mg, 0.029 mmol, 0.063 M) and nitroethane (6.2 μL , 0.086 mmol) gave a 53% yield of **6-Et** after 4 h at room temperature. IR (neat, NaCl; crude reaction mixture containing **6-Et** and TPPO): 1585, 1479, 1434, 1335, 1305, 1198 (s, TPPO), 1118 (s, TPPO) cm^{-1} . ^1H NMR (C_6D_6) of **6-Et**: δ 1.16 (t, 3H, $J = 7.0$ Hz, CH_3), 3.23 (q, 2H, $J = 7.0$ Hz, CH_2), 4.43 (s, 5H, C_5H_5), 7.03 (m, 9H, C_6H_5), 7.72 (m, 6H, C_6H_5).

($\eta^5\text{-C}_5\text{H}_5\text{Co}(\text{PPh}_3)[\eta^1(\text{N})\text{-N}(\text{O})i\text{Pr}]$ (**6-Pr**). In a fashion similar to the reaction above, a dry benzene- d_6 (0.46 mL) solution of **5** (18.6 mg, 0.029 mmol, 0.063 M) and 2-nitropropane (7.7 μL , 0.086 mmol) gave a 38% yield of **6-Pr** after 47 h at room temperature. IR (neat, NaCl; crude mixture of **6-Pr** and TPPO): 1586, 1480, 1435, 1378, 1357, 1309, 1235, 1198 (s, TPPO), 1118 (s, TPPO) cm^{-1} . ^1H NMR (C_6D_6): δ 1.03 (t, 3H, $J = 6.0$ Hz, CH_3), 4.45 (s, 5H, C_5H_5), 4.77 (quint, 1H, $J = 6.5$ Hz, CH), 7.00 (m, 9H, C_6H_5), 7.72 (m, 6H, C_6H_5). ^1H NMR (THF- d_6): δ 0.90 (t, 3H, $J = 6.0$ Hz, CH_3), 4.49 (s, 5H, C_5H_5), 4.94 (quint, 1H, $J = 6.5$ Hz, CH), 7.30 (m, 9H, C_6H_5), 7.61 (m, 6H, C_6H_5).

($[\eta^5\text{-C}_5\text{H}_5\text{Co}]_2[\mu\text{-}\eta^1(\text{N})\text{:}\eta^2\text{-}(\text{N},\text{O})\text{-N}(\text{O})\text{C}_6\text{H}_5]_2$ (**7-Ph**). In the drybox, complex **5** (20 mg, 0.031 mmol, 0.054 M) and toluene (internal standard) were dissolved in dry benzene- d_6 (0.57 mL). Nitrobenzene (9.5 μL , 0.092 mmol, 0.16 M) was added by syringe, and the tube was sealed under a nitrogen atmosphere. After 22 h at room temperature, a ^1H NMR spectrum of the sample indicated a 21% yield of **7-Ph**.

In a preparative-scale experiment, nitrobenzene (0.22 mL, 2.13 mmol) was added by syringe to a benzene (15 mL) solution of **5** (0.455 g, 0.702 mmol). After the mixture was stirred for 23 h at room temperature, the volatiles were evaporated and the residue chromatographed (alumina, 0–5% ethyl acetate/hexanes gradient) to give **7-Ph** (24.0 mg, 7.4% yield) as an air-sensitive black crystalline powder. IR (NaCl, neat): 3053 (m), 2923 (vs), 2853 (s), 1725 (m), 1589 (m), 1525 (w), 1480 (s), 1435 (s), 1345 (m), 1276 (m), 1198 (m), 1118 (s), 1071 (w), 1042 (vw), 1026 (w), 744 (s), 720 (s), 695 (vs) cm^{-1} . ^1H NMR (C_6D_6): δ 4.04 (s, 10H, C_5H_5), 7.02 (m, 6H, C_6H_5), 7.95–8.43 (br m, 4H, C_6H_5). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): δ 81.3, 122.3, 124.6, 129.0, 164.5 (C_i of C_6H_5). HRMS (FAB): calcd for $\text{C}_{22}\text{H}_{20}\text{Co}_2\text{N}_2\text{O}_2$, 462.0189; found, 462.0187.

($[\eta^5\text{-C}_5\text{H}_5\text{Co}]_2[\mu\text{-}\eta^1(\text{N})\text{:}\eta^2\text{-}(\text{N},\text{O})\text{-N}(\text{O})\text{C}_6\text{H}_4\text{C}\equiv\text{CTMS}]_2$ (**7-Ar**). In the drybox, complex **5** (6.3 mg, 0.010 mmol, 0.029 M) and toluene (internal standard) were dissolved in dry benzene- d_6 (0.34 mL). 1-(4-Nitrophenyl)-2-(trimethylsilyl)acetylene (2.9 mg, 0.013 mmol, 0.039 M) was added, and the tube was sealed under a nitrogen atmosphere. After 24 h at room temperature, a ^1H NMR spectrum of the sample indicated a 34% yield of **7-Ar**.

In a preparative-scale experiment, 1-(4-nitrophenyl)-2-(trimethylsilyl)acetylene (50.6 mg, 0.231 mmol) was added to a benzene (15 mL) solution of **5** (0.151 g, 0.233 mmol). After the mixture was stirred for 23 h at room temperature, the volatiles were evaporated and the residue chromatographed (alumina,

0–5% ethyl acetate/hexanes gradient) to give **7-Ar** (12.1 mg, 16% yield) as an air-sensitive black crystalline powder, mp <130 $^\circ\text{C}$ dec. IR (NaCl, neat): 3072 (m), 2953 (vs), 2898 (m), 2153 (s, $\text{C}\equiv\text{C}$), 1725 (m), 1589 (m), 1531 (w), 1483 (s), 1409 (s), 1247 (s), 1233 (w), 1155 (w), 1104 (m), 1021 (m), 838 (s), 801 (s), 723 (s) cm^{-1} . ^1H NMR (C_6D_6): δ 0.28 (s, 18H, TMS), 3.92 (s, 10H, C_5H_5), 7.45 (d, 4H, $J = 8.0$ Hz, C_6H_4), 7.60–8.20 (br m, 4H, C_6H_4). ^1H NMR (CDCl_3): δ 0.26 (s, 18H, TMS), 4.19 (s, 10H, C_5H_5), 7.37 (d, 4H, $J = 8.8$ Hz, C_6H_4), 7.85–8.20 (br m, 4H, C_6H_4). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): δ 0.4, 81.2, 94.6, 106.9, 118 (v br), 119.4, 133.0, 164.6. $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ -0.4, 81.0, 94.4, 105.6, 119 (v br), 118.8, 132.8, 163.7. HRMS (FAB): calcd for $\text{C}_{32}\text{H}_{36}\text{Co}_2\text{N}_2\text{O}_2\text{Si}_2$, 654.0979; found, 654.0975.

X-ray Structure Determination of 6-Me. In the drybox, a single crystal with dimensions $0.25 \times 0.25 \times 0.10$ mm^3 was immersed in Paratone and placed on a glass fiber. Data were collected on a Bruker SMART (APEX) CCD diffractometer by using a graphite monochromator with Mo K α radiation ($\lambda = 0.71073$ \AA) at 100 K. The structure was solved by direct methods and refined by full-matrix least squares on F^2 . All hydrogen atoms were geometrically fixed on their attached atoms during the refinement.²⁴ Table 1 summarizes the crystal data collection and refinement parameters. The ORTEP drawing in Figure 1 illustrates one of the two crystallographically distinct molecules in the unit cell. Data for both molecules in the unit cell are given in the Supporting Information.

X-ray Structure Determination of 7-Ar. A single crystal with dimensions $0.38 \times 0.13 \times 0.09$ mm^3 was immersed in Paratone and placed on a glass fiber. Data were collected on a Bruker SMART (APEX) CCD diffractometer by using a graphite monochromator with Mo K α radiation ($\lambda = 0.71073$ \AA) at 150 K. The crystal was a twin, and the reflections were resolved using GEMINI (v. 1.02) and then integrated using SAINT (v6.35A). The data were massaged by SADABS (v2.04) and TWINABS (v1.02). The structure was then refined by full-matrix least squares on F^2 .²⁴ All hydrogen atoms were geometrically fixed on their attached atoms during the refinement. Table 1 summarizes the crystal data collection and refinement parameters.

Acknowledgment. The support of the National Science Foundation (Grant No. CHE-9975939) is gratefully acknowledged. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

Supporting Information Available: Crystallographic data, as CIF files, for **6-Me** and **7-Ar**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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