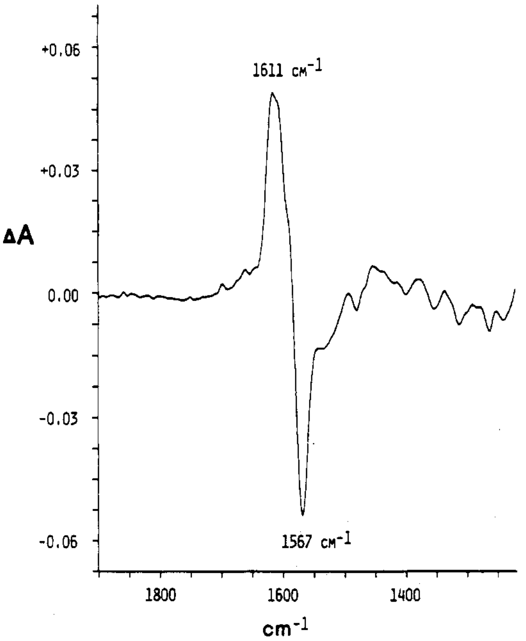

Figure 2. Difference IR absorbance spectrum of complex 4 prepared from $^{12}CO_2$ and $^{13}CO_2$ (KBr) in the ν(CO) region: IR-(4(^{12}C)) - IR(4(^{13}C)).

∠O-C-N are 124.5 (7), 117 (1), and 118.5 (2.1)°, respectively. The average bond lengths of d(C-O) and d(C-N) are 1.255 (7) and 1.415 (21) Å, respectively. These values are near those found in other transition-metal carbamoyl complexes.[18] The C-N bond lengths of the carbamoyl ligands are comparable to that in the organic amide $C_6H_5NH-C(O)CH_3$ (1.426 ± 0.012 Å).[19]

Complex 4 possesses approximate C_{2v} symmetry, with the C_2 axis passing through the bridging carbonyl C=O bond and perpendicular to the Ir-Ir bond. One would therefore predict[20] two ν(CO) bands for the carbamoyl ligands and one ν(CO) band for the bridging carbonyl ligand in the IR spectrum of complex 4. With CO_2, naturally abundant in carbon, the IR spectrum of complex 4 in the ν(CO) region shows three bands at 1611 (sh), 1604 (m), and 1584 (m) cm^{-1}. With $^{13}CO_2$, these bands shift to 1604 (m), 1584 (m), and 1567 (sh) cm^{-1}. Figure 2 is a difference spectrum of the two IR spectra in the ν(CO) region, IR(4(^{12}C))-IR(4(^{13}C)). Figure 2 shows only one significant change of ν(CO) from 1611 to 1567 cm^{-1} caused by carbon-13 labeling. The bands at 1604 and 1584 cm^{-1} remain unchanged. The results of the FTIR difference spectrum have two important implications. First, there are two ν(CO) bands for the carbamoyl carbonyls and one ν(CO) band for the μ-CO ligand, as expected. Second, the μ-CO ligand is derived from carbon dioxide, while the carbamoyl carbonyls are not.

Conclusive evidence for the assignment of the ν(CO) band at 1611 cm^{-1} to the μ-CO ligand of complex 4 comes from GC-MS studies. Complex 4 reacts with 1 equiv of I_2 to liberate the bridging carbonyl ligand.[21,22] One equiv of carbon monoxide is detected by gas chromatography. Reaction of the carbon-13-labeled complex 4 with I_2 gives carbon-13-enriched carbon monoxide, verified by GC-MS analysis.[23] Thus, the bridging carbonyl carbon atom is derived from carbon dioxide.

Our results suggest that during the transformation from the CO_2 adduct 3 to the carbamoyl complex 4, an oxygen atom is transferred from carbon dioxide to an aryl isocyanide leading to an aryl isocyanate according to eq 2. The aryl isocyanate can easily be protonated to form the carbamoyl ligand. The presence of CH_2Cl_2 solvent facilitates this transformation in a complex and as yet unknown mechanism. In the reaction of 3 to afford 4, no free carbon monoxide is released. However, a profile of the CH_2Cl_2 solution IR of complex 3 does reveal the appearence of a new band at 1715 cm^{-1}, suggesting an organic carbonyl compound may also be formed as a byproduct. This byproduct is presumably the destination of the other carbon monoxide formed from the oxygen transfer of carbon dioxide.

While the sequence of reactions leading from 3 to 4 is far from clear, it is certain from $^{13}CO_2$-labeling experiments that the bridging carbonyl of complex 4 is derived from CO_2, while the carbamoyl carbonyls are not. This result is most consistent with net CO_2 oxygen atom transfer followed by CO loss. This represents one example of oxygen atom transfer from carbon dioxide to a coordinated organic ligand.

Acknowledgment. This work was supported by the National Science Foundation (Grant CHE-8411836) and the Materials Research Laboratory at Purdue University.

Supplementary Material Available: Tables of crystal data and conditions for intensity data collection, positional parameters, general temperature factor expressions, bond distances and angles, and least-squares planes and dihedral angles (15 pages); a listing of observed and calculated structure factors (22 pages). Ordering information is given on any current masthead page.

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[18] (a) Breneman, G. L.; Chipman, D. M.; Galles, C. J.; Jacobson, R. A. *Inorg. Chim. Acta* **1969**, *3*, 447. (b) Dell'Amico, D. B.; Calderazzo, F.; Pelizzi, G. *Inorg. Chem.* **1979**, *18*, 1165.

[19] *CRC Handbook of Chemistry and Physics*, 56th ed.; Weast, R. C., Ed; CRC Press: Boca Raton, FL, 1975; p F212.

[20] Cotton, F. A. *Chemical Application of Group Theory*, 2nd ed.; Wiley-Interscience: New York, 1971.

[21] The metal-containing product of this reaction has not been isolated. The high-energy ν(CN) bands at 2275 and 2147 cm^{-1} in the solution IR spectrum indicate a high formal oxidation state for iridiuim.

[22] Iodine oxidations have been used in cobalt carbonyl chemistry to liberate the coordinated CO quantitatively, see: Heck, R. F. *Adv. Organomet. Chem.* **1966**, *4*, 243.

[23] ^{13}C-labeled 4 was disolved in CH_2Cl_2, freeze-pump-thaw degassed three times, and filled with helium gas. One equivalent of I_2 was dissolved in CH_2Cl_2 under helium gas and added to the solution. A gas sample for GC-MS analysis was taken after the mixture was stirred for 1 h.

Activation of Formaldoxime by the Cyclopentadienyldinitrosylchromium Cation[1]

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Summary: Deprotonation of the formaldoxime ligand in $[CpCr(NO)_2\{N(CH_2)OH\}]PF_6$ (Cp = η^5-C_5H_5) by $CpCr(NO)_2Me$ results in the formation of the novel dichromium complex $[\{CpCr(NO)_2\}_2\{\mu,\eta^2\text{-}N(CH_2)O\}]PF_6$ in which the formaldoximato bridge between the two metal centers is not supported by a chromium-chromium bond.

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[1] Organometallic Nitrosyl Chemistry. 34. For part 33, see: Legzdins, P.; Martin, J. T.; Einstein, F. W. B.; Jones, R. H., submitted for publication.

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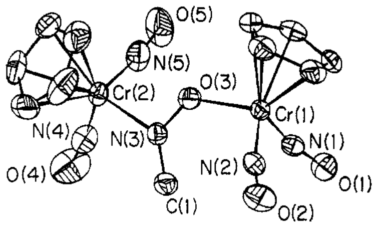
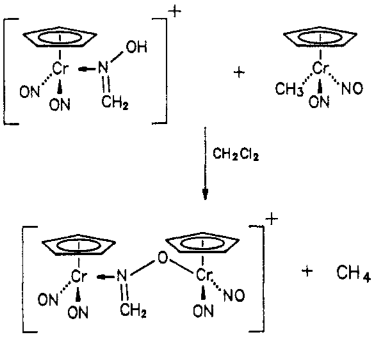


Figure 1. Molecular structure of the $[\{CpCr(NO)_2\}_2\{\mu,\eta^2\text{-}N(CH_2)O\}]^+$ cation as it exists in its BPh_4^- salt. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Cr(1)–N(1) = 1.725 (4), Cr(1)–N(2) = 1.718 (4), Cr(1)–O(3) = 1.956 (3), Cr(2)–N(3) = 2.206 (4), Cr(2)–N(4) = 1.714 (4), Cr(2)–N(5) = 1.706 (5), N(1)–O(1) = 1.169 (5), N(2)–O(2) = 1.174 (5), N(3)–O(3) = 1.348 (5), N(3)–C(1) = 1.282 (4), N(4)–O(4) = 1.160 (5), N(5)–O(5) = 1.170 (6), N(1)–Cr(1)–N(2) = 94.5 (2), N(1)–Cr(1)–O(3) = 103.6 (2), N(3)–Cr(2)–N(4) = 99.9 (2), N(4)–Cr(2)–N(5) = 94.2 (2), Cr(1)–N(1)–O(1) = 165.7 (4), Cr(1)–O(3)–N(3) = 128.5 (3), Cr(2)–N(3)–O(3) = 109.3 (3), Cr(2)–N(4)–O(4) = 171.7 (4).

The activation of small molecules toward new reactivity patterns by coordination to organo-transition-metal centers has been the focal point of much research for a number of years.[2] However, one class of small molecules that has received scant attention in this regard consists of the neutral oximes $R_2C{=}NOH$, where R = alkyl, aryl, or H.[3] In this communication, we wish to report that (A) coordination of the simplest oxime, formaldoxime ($H_2C{=}NOH$), to the chromium center of the 16-electron $[CpCr(NO)_2]^+$ cation (Cp = $\eta^5\text{-}C_5H_5$) activates it toward deprotonation and (B) when this deprotonation is effected with $CpCr(NO)_2Me$, an unprecedented type of an oximato-bridged bimetallic complex results. The specific transformation being considered is presented in eq 1.



In a typical experiment, solid $[CpCr(NO)_2\{N(CH_2)OH\}]PF_6$[4] (0.367 g, 1.00 mmol) was added to a CH_2Cl_2 solution (25 mL) of $CpCr(NO)_2Me$[5] (0.192 g, 1.00 mmol), and the mixture was stirred vigorously for 10 days at ambient temperature under an atmosphere of N_2. [The evolution of CH_4 was established by GCMS.[6]] Addition of hexanes (100 mL) to the final green reaction solution resulted in the precipitation of $[\{CpCr(NO)_2\}_2\{\mu,\eta^2\text{-}N(CH_2)O\}]PF_6$ as a green, diamagnetic solid in 85% yield.[7] The isolated solid is air-stable and is most soluble in good solvating solvents such as nitromethane.[8]

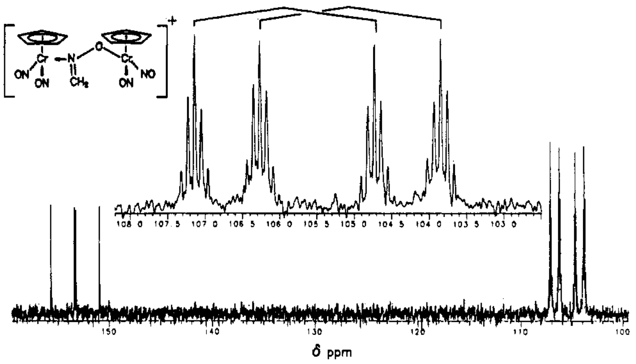


Figure 2. The 75.429-MHz ^{13}C NMR spectrum of $[\{CpCr(NO)_2\}_2\{\mu,\eta^2\text{-}N(CH_2)O\}]PF_6$ in CD_3NO_2 at 20 °C. The inset contains an expansion of the signals due to the Cp carbons at δ 105.94 and 105.06.

Single-crystal X-ray crystallographic analysis of the dichromium cation (as its BPh_4^- salt)[9] revealed a new type of an oximato-bridged molecular structure (Figure 1).[10] The intramolecular dimensions of the bimetallic cation indicate two structurally normal $CpCr(NO)_2$ groups[11] held together only by single bonds to the N and O atoms of the formaldoximato ligand, respectively. All other structurally characterized bimetallic complexes having an oximato ligand spanning the two metal centers possess a metal–metal bond.[12,13] The spectroscopic properties of the $[\{CpCr(NO)_2\}_2\{\mu,\eta^2\text{-}N(CH_2)O\}]^+$ cation (as its more soluble PF_6^- salt)[7] are readily interpretable in terms of its solid-state molecular structure, a fact which indicates that the basic dichromium structural units persist in solutions. Particularly interesting is the ^{13}C NMR spectrum of the cation in CD_3NO_2 (Figure 2) which exhibits two Cp carbon signals at δ 105.94 and 105.06. Each appears as a doublet of quintets because of short-range $^{13}C\text{–}^1H$ coupling of 182 Hz and long-range coupling of 6.5 Hz to the four other protons of the Cp ring. Furthermore, the signal due to the methylene carbon of the bridging formaldoximato group appears as a doublet of doublets at δ 153.33 ($^1J_{^{13}C\text{–}^1H}$ = 185, 173 Hz), the coupling constants being fully consistent with this carbon retaining its sp^2 hybridization.

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(2) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987.

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(4) Legzdins, P.; Wassink, B.; Einstein, F. W. B.; Willis, A. C. *J. Am. Chem. Soc.* **1986**, *108*, 317.

(5) Hoyano, J. K.; Legzdins, P.; Malito, J. T. *J. Chem. Soc., Dalton Trans.* **1975**, 1022.

(6) Using a DBI-30W (5-μm) column at 5 °C and a Kratos MS-80 mass spectrometer.

(7) Anal. Calcd for $C_{11}H_{12}N_5O_5PF_6Cr_2$: C, 24.31; H, 2.21; N, 12.89. Found: C, 24.22; H, 2.24; N, 12.71. IR (Nujol): ν_{NO} 1832 (s), 1809 (s), 1716 (s), 1700 (s) cm^{-1}; ν_{NC} 1567 (w) cm^{-1}. IR (CH_2Cl_2): ν_{NO} 1833 (s), 1811 (s), 1731 (s), 1709 (s) cm^{-1}. ^1H NMR (CD_2Cl_2) δ 7.25 (d, 1 H, $-ONCH_AH_B$, $^2J_{^1H_A\text{–}^1H_B}$ = 6.3 Hz), 7.13 (d, 1 H, $-ONCH_AH_B$), 5.81 (s, 5 H, C_5H_5), 5.74 (s, 5 H, C_5H_5). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 151.41 (s, CH_2), 104.59 (s, C_5H_5), 103.76 (s, C_5H_5). ^{13}C NMR (CD_3NO_2): δ 153.33 (dd, CH_AH_B, $^1J_{^{13}C\text{–}^1H}$ = 185, 173.4 Hz), 105.94 (dq, C_5H_5, $^1J_{^{13}C\text{–}^1H}$ = 182.2 Hz, $^nJ_{^{13}C\text{–}^1H}$ = 6.5 Hz), 105.06 (dq, C_5H_5, $^1J_{^{13}C\text{–}^1H}$ = 182.6 Hz, $^nJ_{^{13}C\text{–}^1H}$ = 6.5 Hz).

(8) Drago, R. S. *Pure Appl. Chem.* **1980**, *52*, 2261.

(9) X-ray diffraction data for $[\{CpCr(NO)_2\}_2\{\mu,\eta^2\text{-}N(CH_2)O\}]BPh_4$: monoclinic; space group $P2_1/c$; a = 10.865 (3) Å, b = 18.360 (2) Å, c = 17.402 (5) Å, β = 101.13 (2)°; V = 3406.1 $Å^3$; Z = 4; absorption coefficient = 6.68 cm^{-1}; diffractometer, Enraf-Nonius CAD4F; radiation, Mo Kα, graphite monochromated ($\lambda(K\alpha_1)$ = 0.709 30 Å); temperature = 212 K; scan range = $0° \leqslant 2\theta \leqslant 50°$; reflections = 3962 with $I \geqslant 2.5\sigma(I)$; R = 0.033, R_w = 0.035; GOF = 1.1158; number of parameters = 531. All atoms, including H atoms, were refined.

(10) Thermal ellipsoids enclose 50% probabilities. Davies, E. K. *CHEMGRAF Users' Guide*; Chemical Crystallography Laboratory, University of Oxford: Oxford, England, 1983.

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(13) For an example of a monometallic complex containing a bidentate oximato ligand, see: Khare, G. P.; Doedens, R. J. *Inorg. Chem.* **1977**, *16*, 907.

The occurrence of reaction 1[14] is of fundamental significance since free oximes such as diacetyl monoxime (pK_a = 9.3)[15a] or even carboxylic acids such as *p*-fluorobenzoic acid (pK_a = 4.14)[15b] do not react with CpCr(NO)$_2$Me under identical experimental conditions. The role of the electrophilic [CpCr(NO)$_2$]$^+$ cation in activating formaldoxime by coordination is thus to increase substantially its Brønsted acidity above that which it possesses in its free state. Once activated, the bound formaldoxime can then undergo deprotonation by CpCr(NO)$_2$Me to afford the observed products.[16]

The utility of the CpCr(NO)$_2$$^+$ cation for effecting the activation of other small molecules of synthetic importance is currently being investigated.

Acknowledgment. We are grateful to the Natural Sciences and Engineering Research Council of Canada for support of this work in the form of grants to P.L. and F.W.B.E. and to the University of British Columbia for the award of a graduate fellowship to G.B.R.-A. We also thank Professor Ross Stewart for helpful discussions.

Supplementary Material Available: Tables of fractional coordinates and isotropic and anisotropic thermal parameters for [{CpCr(NO)$_2$}$_2${μ,η^2-N(CH$_2$)O}]BPh$_4$ (7 pages); a listing of structure factors for [{CpCr(NO)$_2$}$_2${μ,η^2-N(CH$_2$)O}]BPh$_4$ (33 pages). Ordering information is given on any current masthead page.

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[14] The occurrence of reaction 1 explains why [{CpCr(NO)$_2$}$_2$[μ,η^2-N-(CH$_2$)O}]PF$_6$ is formed as a byproduct during the synthesis of [CpCr-(NO)$_2${N(CH$_2$)OH}]PF$_6$[4] from CpCr(NO)$_2$Me and NOPF$_6$ in CH$_2$Cl$_2$ if (a) an excess of CpCr(NO)$_2$Me is used or (b) the insoluble NOPF$_6$ is not finely ground (in effect causing (a) locally).

[15] (a) Krueger, P. J. In *The Chemistry of the Hydrazo, Azo and Azoxy Groups*; Patai, S., Ed.; Wiley-Interscience: New York, 1975; Part 1, p 167. (b) Dean, J. A. *Handbook of Organic Chemistry*; McGraw-Hill: New York, 1987; Section 8.

[16] Cp$_2$Zr(Cl)Me has also been employed recently to deprotonate other organic groups bound to organo-transition-metal centers.[17]

[17] Tso, C. T.; Cutler, A. R. *J. Am. Chem. Soc.* **1986**, *108*, 6069.

Photochemical Generation of Cyclopropenylsilylenes

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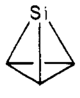
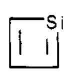
Received February 27, 1987

Summary: Two cyclopropenyltrisilanes have been prepared by the reaction of tri-*tert*-butylcyclopropenium tetrafluoroborate with silyllithium reagents. The 254-nm photolysis of one of these compounds in the presence of ethanol gives trapping products indicative of an initially generated cyclopropenylsilylene.

The SiC$_3$H$_4$ isomer surface, which includes silatetrahedrane (1) and silacyclobutadiene (2), is a potential paradigm for the interplay of ring strain and antiaromatic delocalization in organosilicon molecules. Calculations by Gordon suggest that silacyclobutadiene is the most stable of the isomers, 33.3 kcal mol^{-1} more stable than silatetrahedrane and 56.3 kcal mol^{-1} more stable than a silyne–alkyne pair.[1] A sophisticated calculation by Schaeffer on the structure and electronic properties of singlet and triplet silcyclobutadiene has also appeared.[2] Despite theoretical interest in these molecules, there is little experimental evidence for their existence.[3]



1



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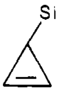
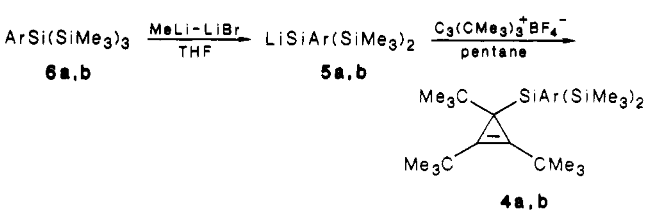


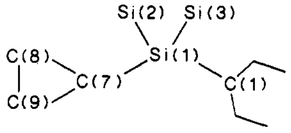
3

Scheme I[a]



[a] **a**, Ar = Ph; **b**, Ar = Mes (mesityl; 2,4,6-trimethylphenyl).

Table I. X-ray Structure of 4a: Selected Bond Lengths and Angles



Bond Lengths (Å)

Si(1)-Si(2)	2.396 (2)	C(7)-C(8)	1.546 (6)
Si(1)-Si(3)	2.398 (2)	C(7)-C(9)	1.536 (6)
Si(1)-C(1)	1.893 (5)	C(8)-C(9)	1.284 (6)
Si(1)-C(7)	1.940 (4)		

Bond Angles (deg)

C(8)-C(7)-C(9)	49.3 (3)
C(7)-C(8)-C(9)	64.9 (3)
C(7)-C(9)-C(8)	65.8 (3)

In an effort to synthesize analogs of 1 and 2, we have sought to generate derivatives of yet another SiC$_3$H$_4$ species, cyclopropenylsilylene (3). Similar low-valent species, most notably cyclopropenyl carbenes and nitrenes, undergo facile rearrangements to give cyclobutadienes and azetes, respectively.[4] Accordingly, cyclopropenylsilylenes may prove to be convenient sources of either 1 or 2. We report herein the synthesis of two photochemical precursors of highly substituted cyclopropenylsilylenes, a solid-state structure, and preliminary photochemistry of one of these compounds.

A convenient route to organosilylenes is the photolysis of 2-aryltrisilanes.[5] Two cyclopropenylaryltrisilanes, **4a** and **4b**, were prepared by the respective addition of silyllithium reagents **5a** and **5b** to a pentane slurry of tri-*tert*-butylcyclopropenium tetrafluoroborate at room temperature. Filtration and removal of solvent in vacuo gave **4a** and **4b** in 65% and 68% yields, respectively. The corresponding lithium reagents were prepared by the action of MeLi–LiBr on the tetrasilanes **6a** and **6b** as shown in Scheme I.

Compounds **4a** and **4b** are white crystalline solids that are stable in refluxing xylene and unreactive toward mild acids. Both **4a** and **4b** show a characteristic cyclopropene C=C stretch at 1815 and 1810 cm^{-1}, respectively. Other spectral data are consistent with the proposed structures.[6]

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[4] For pertinent examples, see: Masamune, S.; Nakamura, M.; Suda, M.; Ono, H. *J. Am. Chem. Soc.* **1973**, *95*, 8481–8483. Vogelbacher, U.-J.; Regitz, M.; Mynott, R. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 842–843.

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