reveals it to undergo a reversible one-electron reeduction process in aprotic solvents at Hg and Pt electrodes.[11a,b] At a Pt electrode at 200 mV/s in THF, $CpCo(CO)_2$ is reduced at an E_{pc} of −2.23 V vs. $Cp_2Fe^{0/+}$. In contrast, cyclic voltammetry on Ia under identical conditions indicates that reduction of this complex is a two-electron, "ECE_{rev}"-type process.[11c] At 200 mV/s, the initial reduction wave peak position of Ia occurs at −1.76 V vs. ferrocene(0/+). The 0.47 V less negative reduction potential of Ia is consistent with the proposal that benzoyl isocyanide is a stronger π-acceptor than CO.

The voltammetric behaviors of Ib and Ic are very similar to that of Ia. The initial cathodic peak under these conditions for Ic is at −2.38 V. The shift in E_{pc} to a substantially more negative value on going from Ia to Ic shows that the phenyl group of the benzoyl isocyanide ligand is conjugated to the acyl isocyanide moiety. The implication is that benzoyl isocyanide is a better π-acceptor ligand than is the saturated acyl isocyanide.

A similarity between Ia and $CpCo(CO)_2$ is in their Lewis basicity. $CpCo(CO)_2$ reacts with $HgCl_2$ to produce a Lewis acid–base complex containing a Co–Hg bond.[12] When treated with $HgCl_2$, dark red-brown Ia is transformed into a golden yellow powder in a manner totally analogous to $CpCo(CO)_2$. Elemental analysis indicates that this is a monoadduct.[13] $Ia{\cdot}HgCl_2$ appears to be significantly more labile than $CpCo(CO)_2{\cdot}HgCl_2$ in that it cannot be recrystallized successfully, dissociating in solution and also when ground as a solid as in the preparation of a mull for IR study. This is consistent with the better π-acceptor ability of benzoyl isocyanide resulting in Ia being a weaker Lewis base than is $CpCo(CO)_2$.

We have evidence that other new acyl isocyanide complexes can be prepared from reactive metal carbonyls in the same manner. Thus, solutions of benzoyl isocyanide react with $C_5Me_5Rh(CO)_2$ at ambient temperature and with $Mn(CO)_5Br$ in refluxing THF. The products of these reactions are currently being characterized.[14] The reaction chemistry of these low-valent acyl isocyanide complexes is currently under study and will be reported on at a later date.

Acknowledgment. This work was supported by the NSF (CHE-8209006). Mass spectra were obtained on the NIH-funded (GMO-7261) instrument in the Brandeis Biochemistry department.

Supplementary Material Available: (i) Complete details of data collection, solution, and refinement of structure and tables of (ii) atomic coordinates, (iii) anisotropic thermal parameters, (iv) H atom coordinates, (v) bond lengths and angles, (vi) least-squares planes, and (vii) phenyl ring bond lengths and angles (10 pages); a list of (viii) observed and calculated structure amplitudes (5 pages). Ordering information is given on any current masthead page.

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[11] (a) Schore, N. E.; Ilenda, C. S.; Bergman, R. G. *J. Am. Chem. Soc.* **1977**, *99*, 1781–7. (b) Stuhl, L. S., unpublished results. (c) Cyclic voltammetry was performed at an IBM Pt disk electrode, with a ferrocene-calibrated silver wire quasi-reference electrode. Voltage control and monitoring were provided by a PAR 173/175 combination linked to a Bascom-Turner digital recorder. Solutions were 1×10^{-3} M Ia in 0.2 M Bu_4NBF_4/THF solution under an argon atmosphere. Data were recorded at scan rates of 50–500 mV/s. Details of these experiments will be provided in a separate publication.

[12] Cook, D. J.; Dawes, J. L.; Kemmitt, D. W. *J. Chem. Soc. A* **1967**, 1548–51.

[13] ATR-IR (KRS-5 plate, 45° windows) 2100 (s, br), 1775 (w) 1700 (s), 1595 (s) cm^{-1}. Anal. Calcd for $C_{21}H_{15}N_2O_2CoHgCl_2$ (Found): C, 38.35 (38.45); H 2.30 (2.80); Co, 8.96 (8.51). We have not been able to purify this material further by recrystallization.

[14] There is an immediate reaction between $C_5Me_5Rh(CO)_2$ and *p*-methylbenzoyl isocyanide in MeCN, the solution color changing from orange to burgundy, followed by a slower change to a browner red similar to the solution color of Ia. Evidence for the formation of $CpRhL_2$ is the appearance of IR bands at 1968 (s),1734 (w), 1683 (m), and 1613 (m) cm^{-1}. This material has not yet been successfully purified. $MnBr(CO)_5$ reacts with excess benzoyl isocyanide in refluxing THF to produce a solution having an obviously deeper orange color than that of the starting complex. Evidence for coordinated benzoyl isocyanide is new IR bands at 1985 (s), 1963 (s), 1724 (vs), 1602 (m), and 1586 (w) cm^{-1}, as well as several weak bands and shoulders which may also be assignable to isocyanide complexes. This reaction produces a mixture of several complexes which can be incompletely separated from each other by chromatography on silica; the separation is complicated by the partial decomposition of the complexes on the column (other absorbents behave similarly with poorer resolution or excessive retention). The chromatographed fractions yield an assortment of orange or yellow oils which have so far defied efforts to induce crystallization. The band at 1968 cm^{-1} in the Rh reaction mixture and the bands at 1985 and 1963 cm^{-1} in the Mn reaction display the characteristic breadth of coordinated acyl isocyanide adsorptions, which are generally 2–3 times broader than carbonyl stretches in the same frequency range.

Formation of a Thioformaldehyde Ligand by the Addition of Sulfur to a Methylene Ligand in a Cluster Complex. The Synthesis and Structural Characterizations of the Clusters $Os_3(CO)_n(\mu\text{-}SCH_2)$ (n = 10, 11)

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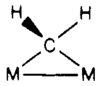
Summary: Reaction of $Os_3(CO)_{11}(\mu\text{-}CH_2)$ with ethylene sulfide leads to transfer of sulfur to the methylene group in the cluster complex and formation of the new complexes $Os_3(CO)_{11}(\mu\text{-}SCH_2)$ and $Os_3(CO)_{10}(\mu_3\text{-}SCH_2)$ which contain doubly and triply bridging thioformaldehyde ligands, respectively.

A great deal of interest has been focused on the chemistry of the bridging methylene ligand, A, that is found in polynuclear transition-metal complexes.[1] This ligand has been shown to engage in carbon–carbon bond formation to CO[2] and to unsaturated hydrocarbons,[3,4] and it is believed to be an important intermediate in the reactions involved in Fischer–Tropsch catalysis.[5] Sulfur is one of the most notorious of the poisons of the Fischer–Tropsch and related catalytic processes.[6] We now wish to report the first example of the addition of sulfur to a bridging methylene ligand in a cluster complex and on the structure determinations of the resultant products.[7]



A

The reaction of 20.0 mg of $Os_3(CO)_{11}(\mu\text{-}CH_2)$ with 50 μL of ethylene sulfide in 15 mL of refluxing cyclohexane

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[1] (a) Herrmann, W. A. *Adv. Organomet. Chem.* **1982**, *20*, 159. (b) Herrmann, W. A. *Pure Appl. Chem.* **1982**, *54*, 65.

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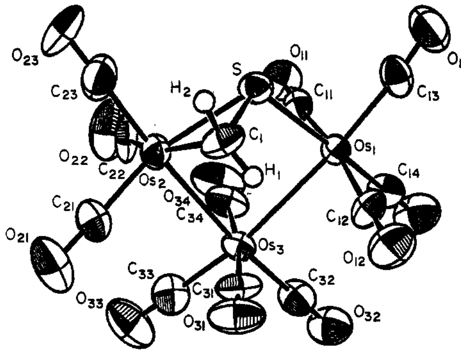

Figure 1. An ORTEP diagram of the molecular structure of $Os_3(CO)_{11}(\mu\text{-}SCH_2)$ (1) showing 50% probability thermal ellipsoids. The ellipsoids on the hydrogen atoms have been reduced for clarity.

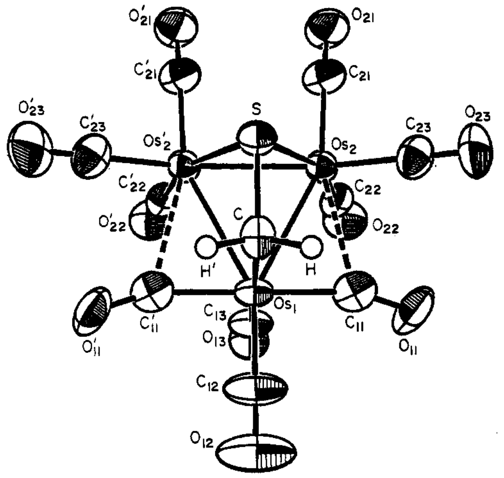

Figure 2. An ORTEP diagram of the molecular structure of $Os_3(CO)_{10}(\mu_3\text{-}SCH_2)$ (2) showing 50% probability thermal ellipsoids. The ellipsoids on the hydrogen atoms have been reduced for clarity.

solvent for 25 min yielded the new compounds $Os_3(CO)_{11}(\mu\text{-}SCH_2)$ (1, 5.0 mg, 24% yield) and $Os_3(CO)_{10}(\mu_3\text{-}SCH_2)$ (2, 3.1 mg, 15% yield).[7] These products have been characterized by IR and ^1H NMR spectroscopies[9] and by elemental and single-crystal X-ray diffraction analyses.[11,12] An ORTEP drawing of the molecular structure of 1 is shown in Figure 1.[13] The molecule consists of an open triangular cluster of three osmium atoms with two osmium–osmium bonds, Os(1)–Os(3) = 2.951 (1) Å and Os(2)–Os(3) = 2.948 (1) Å. A thioformaldehyde ligand, $H_2C{=}S$, bridges the nonbonded pair of osmium atoms Os(1)···Os(2) = 3.859 (1) Å. The sulfur atom bridges both metal atoms, Os(1)–S = 2.443 (4) Å and Os(2)–S = 2.394 (4) Å, while the carbon atom is coordinated only to Os(2), Os(2)–C(1) = 2.16 (2) Å. The carbon–sulfur bond at 1.77 (2) Å is slightly shorter than a carbon–sulfur single bond, 1.80–1.82 (Å).[14] The thioformaldehyde ligand could be viewed as π-bonded to Os(2) and σ-bonded to Os(1). A similarly coordinated thioformaldehyde ligand was observed in the cluster complex $Os_3(CO)_9(PMe_2Ph)(\mu\text{-}SCH_2)(\mu_3\text{-}S)$.[15] The hydrogen atoms were located as shown in the figure. In the ^1H NMR spectrum they appear as an AB quartet, $J_{H-H} = 5.81$ Hz.[9]

An ORTEP diagram of the molecular structure of 2 is shown in Figure 2.[11,16] In the solid state the molecule contains a crystallographically imposed plane of symmetry that passes through the atoms Os(1), C, S, and the two carbonyl ligands C(12)–O(12) and C(13)–O(13). The molecule consists of a closed triangular cluster of three osmium atoms, Os(1)–Os(2) = 2.862 (1) Å and Os(2)–Os(2′) = 2.745 (2) Å. A triply bridging thioformaldehyde ligand symmetrically bridges the three metal atoms with the sulfur atom bridging Os(2)–Os(2′), Os(2)–S = 2.415 (6) Å, and the carbon atom bonded only to Os(1), Os(1)–C = 2.14 (3) Å. The C–S distance of 1.82 (3) Å is typical of a carbon–sulfur single bond.[14] It is slightly longer than that observed in 1 and shorter than the 1.869 (6) Å value found for the triply bridging thioformaldehyde ligand in the open cluster $Os_3(CO)_8(PMe_2Ph)(\mu_3\text{-}SCH_2)(\mu_3\text{-}S)_2$.[15] The hydrogen atom on the carbon atom of the thioformaldehyde ligand was located in a credible position, C–H = 1.02 Å and H–C–H = 121°, in a difference Fourier map. All the carbonyl ligands are of a linear terminal type except the C(11)–O(11), C(11′)–O(11′) pair on Os(1) which are semibridges to Os(2) and Os(2′). The reason for this can be attributed to the electron-rich character of Os(1) which produces an excess of electron donation to the atoms Os(2) and Os(2′).[17]

The stoichiometry of 1 and 2 suggested that 2 could be formed from 1 simply by loss of CO. Indeed, when 1 was refluxed in hexane solvent for 5 h, it was converted into 2 quantitatively. Interestingly, the decarbonylation is reversible. When solutions of 2 were placed under CO (55

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[7] Gladysz has recently shown that sulfur can be transferred from cyclohexene sulfide to the terminal methylene group in the mononuclear metal complex $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)({=}CH_2)^+$ to yield a π-bonded thioformaldehyde ligand in the product $(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^2\text{-}H_2C{=}S)^+$.[8]

[8] Buhro, W. E.; Patton, A. T.; Strouse, C. E.; Gladysz, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 1056.

[9] The minor product of this reaction is $Os_3(CO)_9(\mu_3\text{-}S)_2$ which is obtained in 8% yield. Compounds 1 and 2 were isolated by TLC on silica gel plates by eluting with hexane solvent. IR (ν(CO), cm^{-1}, in hexane): for 1, 2126 w, 2077 s, 2055 m, 2049 s, 2040 m, 2028 m, 2011 w, 1997 m, 1992 m, 1976 m, 1970 w; for 2, 2104 w, 2068 s, 2056 s, 2034 m, 2016 w, 2002 m. ^1H NMR (δ in $CDCl_3$): for 1, 3.74 (d, $J_{H-H} = 5.81$ Hz), 3.56 (d, $J_{H-H} = 5.81$ Hz); for 2, 1.69 (s). Satisfactory elemental analyses (C, H) have been obtained.

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[11] Diffraction measurements were made on a Rigaku AFC6 automatic diffractometer by using Mo Kα radiation. Structure solutions and refinements were performed on a Digital Equipment Corp. MICROVAX I computer by using the Molecular Structure Corp. TEXSAN program library. The data were corrected for absorption.

[12] Crystals of 1 were grown from $CHCl_3$/cyclohexane solution at −20 °C. Compound 1 crystallizes in the monoclinic crystal system, space Group $P2_1/n$, with $a = 8.262$ (2) Å, $b = 14.092$ (5) Å, $c = 16.315$ (4) Å, $\beta = 102.02$ (2)°, $Z = 4$, and $\rho_{calcd} = 3.31$ g/cm^3. The structure was solved by direct methods (MULTAN) and was refined (2384 reflections) to the final values of the residuals $R = 0.0437$ and $R_w = 0.0524$.

[13] Selected interatomic distances (Å) and angles (deg) for 1 are as follows: Os(1)···Os(2) = 3.859 (1), Os(1)–Os(3) = 2.951 (1), Os(2)–Os(3) = 2.948 (1), Os(1)–S = 2.443 (4), Os(2)–S = 2.394 (4), Os(1)···C(1) = 3.48 (2), Os(2)–C(1) = 2.16 (2), Os(3)···C(1) = 3.72 (2), S–C(1) = 1.77 (2); Os(1)–S–Os(2) = 105.8 (2), Os(2)–C(1)–S = 74.3 (6), Os(2)–S–C(1) = 60.2 (6).

[14] (a) Frank, G. W.; Degen, P. J. *Acta Crystallogr. Sect. B: Struct. Crystallogr. Cryst. Chem.* **1973**, *B29*, 1815. (b) Vallee, G.; Busetti, V.; Mammi, M.; Carazzolo, G. *Ibid.* **1969**, *B25*, 1432. (c) Vallee, G.; Busetti, V.; Mammi, M.; Carazzolo, G. *Ibid.* **1969**, *B25*, 1631. (d) Fleming, J. E.; Lynton, H. *Can. J. Chem.* **1967**, *45*, 353. (e) Cunningham, C. G., Jr.; Boyd, A. W.; Meyers, R. J.; Gwinn, W. D.; LeVan, W. I., *J. Chem. Phys.* **1951**, *19*, 676.

[15] Adams, R. D.; Golembeski, N. M.; Selegue, J. P. *J. Am. Chem. Soc.* **1981**, *103*, 546.

[16] Crystals of 2 were grown from $CHCl_3$/cyclohexane solution at −20 °C. Compound 2 crystallizes in the orthorhombic crystal system, space group *Pnma*, with $a = 13.721$ (3) Å, $b = 13.899$ (5) Å, $c = 8.908$ (2) Å, $Z = 4$, and $\rho_{calcd} = 3.50$ g/cm^3. The structure was solved by direct methods (MULTAN) and was refined (1138 reflections) to the final values of the residuals $R = 0.0454$ and $R_w = 0.0474$. Selected interatomic distances (Å) and angles (deg) for 2 are as follows: Os(1)–Os(2) = 2.862 (1), Os(2)–Os(2′) = 2.745 (2), Os(1)–C = 2.14 (3), Os(2)–S = 2.415 (6), S–C = 1.82 (3), Os(2)···C(11) = 2.572, C–H = 1.02; Os(2)–S–Os(2′) = 69.3 (2), Os(2)–S–C = 94.8 (7), Os(1)–C–S = 103 (1), Os(1)–C(11)–O(11) = 162 (2).

[17] Cotton, F. A. *Prog. Inorg. Chem* **1976**, *21*, 1.

atm/85 °C) for 6 h, compound 1 was reformed quantitatively.

The facile carbon–sulfur bond formation that occurred in the formations of 1 and 2 suggests that similar processes could be important on sulfur-contaminated metal surfaces and that the interactions of sulfur with the key hydrocarbyl intermediate formed in Fischer–Tropsch and related catalytic processes may play a role in the inhibition of these reactions by sulfur.

Acknowledgment. These studies were supported by the Office of Basic Energy Sciences of the U.S. Department of Energy. We wish to thank Johnson Matthey Inc. for a loan of osmium tetraoxide. NMR measurements were made on a Brüker AM-300 spectrometer purchased with funds from the National Science Foundation under Grant CHE-8411172.

Supplementary Material Available: Tables of crystal data, positional and thermal parameters, and selected interatomic distances and angles (11 pages); tables of structure factor amplitudes (26 pages). Ordering information is given on any current masthead page.

Alkyne Reactions with Cyclopalladated Complexes

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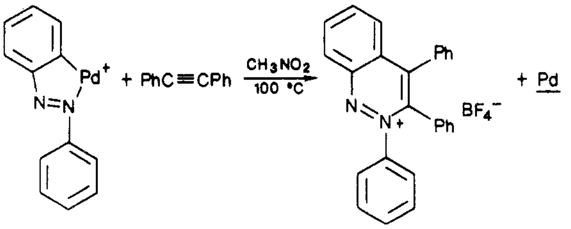
Summary: A general scheme is proposed for reactions of cyclopalladated complexes with alkynes. Successive insertions of alkyne units form a series of complexes which in turn may reductively eliminate palladium or rearrange. Four types of products are known, additional examples of one type and two new types are reported in our study of reactions of ionic cyclopalladated complexes. These last reactions are useful for preparing 2-substituted cinnolinium salts and isoquinolinium salts. A double alkyne insertion occurs with some complexes to form naphthalene derivatives, and a cyclopentadiene ring is formed from a triple alkyne insertion in another example.

The literature reports several reactions of alkynes with cyclopalladated complexes. Cyclopalladated complexes of *N*,*N*-dimethylbenzylamine,[1] 8-methylquinoline,[1] benzo[*h*]quinoline,[1] and 2-benzylpyridine,[2] for example, generally have given various organopalladium compounds as products with alkynes. The reported reactions were all carried out with the covalent cyclopalladated chloride dimers, acetate dimers, or palladium complexes having two chelating organic ligands.[3] We have now found that converting the cyclopalladated complexes to the presumed ionic tetrafluoroborates significantly activates the complexes and reactions with alkynes occur even at room temperature. Different types of products than previously reported are obtained in some of these reactions.

Our initial results combined with the literature reports strongly suggest a general reaction scheme that indicates the relationships between all of the various products so far obtained from the reactions. Scheme I below shows the proposed reactions illustrated with the *N*,*N*-dimethylbenzylamine complex. A series of single alkyne insertions is proposed which yield palladium complexes at each step. These complexes either may insert another alkyne unit or may undergo palladium(0) elimination or rearrangements to other products. Substantial evidence now exists to support the proposed steps although not all with the same cyclopalladated complex. Which of the possible paths a given complex will take in reacting with an alkyne will depend upon steric and electronic factors in both the complex and alkyne and upon the concentration of the reacting alkyne as well as upon the reaction temperature if the activation energies of the various possible reactions are significantly different.

Complexes of the type II,[1,3] IV,[1] and V[2] have been reported to be formed in alkyne reactions. One product of type III has been reported employing hexafluorobutyne as the reactant[1] (demethylation also occurred in the example), and we now report several more examples of this reaction. We have also found examples of the formation of product VII and complex IX.

Treatment of the cyclopalladated chloro dimer from azobenzene[5] with silver tetrafluoroborate in nitromethane solution rapidly causes silver chloride to precipitate and a bright red solution is formed. Filtration and evaporation of the solvent leaves a viscous red oil which, so far, has resisted attempts at crystallization. The less reactive bis(acetonitrile) complex, however, is easily obtained as stable yellow crystals from acetonitrile solution. The reaction of the "(azobenzene)palladium tetrafluoroborate" in nitromethane with excess diphenylacetylene at room temperature led to the formation of 35% of 2,3,4-triphenylcinnolinium tetrafluoroborate and, presumably, polyinsertion products as viscous, nonseparable oils. The yield of the cinnolinium salt is 87% if the diphenylacetylene (0.8 M in nitromethane) is added slowly to the stirred palladium salt in nitromethane solution (~0.13 M) at 100 °C (over a period of 3.5 h; eq 1). (This procedure eliminates the competition of $k_2[\mathrm{PhC{\equiv}CPh}]$ with k_1 in Scheme I.) The structure of the product was determined by X-ray crystallography. Similar yields of the expected cinnolinium salts were obtained from 3-hexyne (83%) and from dimethyl acetylenedicarboxylate (80%). This reaction is a useful, new method for preparing some of the very rare, 2-substituted cinnolinium salts.



(1)

The same type of reaction occurs between 3-hexyne and cyclopalladated *N*-benzylidene-*o*-toluidine[6] and *N*-

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