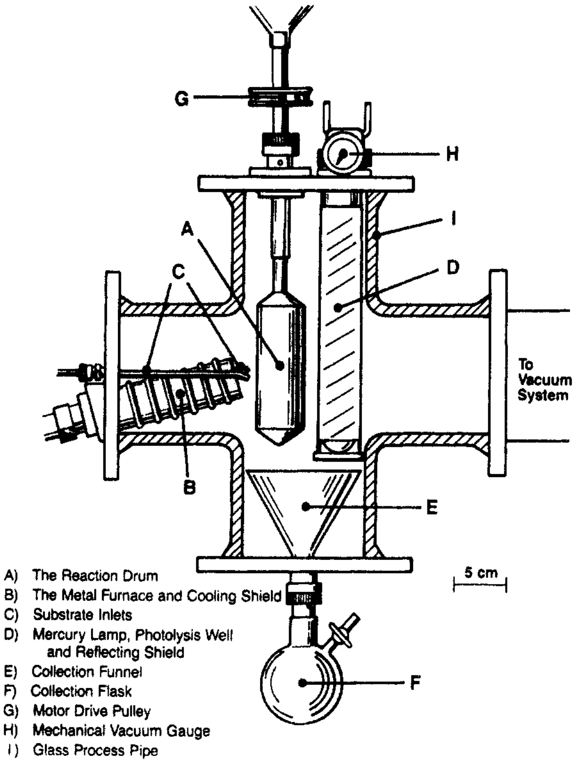
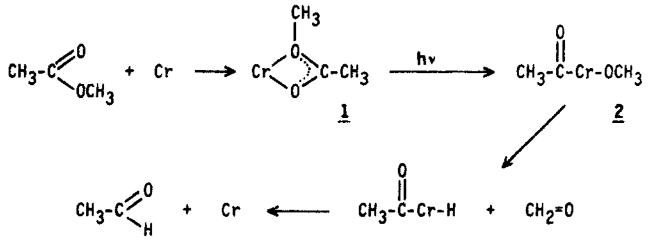


Figure 1. Photochemical metal vapor reactor.

Scheme I



The reactor used in this study is illustrated in Figure 1. This apparatus may be used to cocondense metal vapor with any sufficiently volatile organic compound onto a stainless-steel drum at 77 K. The drum is rotated during the cocondensation to assure that the cocondensate is uniformly deposited. Photolysis is carried out during the cocondensation using a 450-W medium-pressure Hg arc lamp. All reactions are carried out at 10^{-5} torr. Products may be readily collected in the receiving flask as the matrix is allowed to warm.

When the cocondensate of methyl acetate and chromium vapor is photolyzed, the major organic product is acetaldehyde. Under the most favorable conditions (700/1 molar ratio of ester to metal) acetaldehyde is produced in a 60% yield (based on metal deposited).[9] Several other minor products are isolated from the reaction including methanol, methyl formate, and formaldehyde. Cocondensation of the ester with chromium vapor in the absence of photolysis yields only trace amounts of methanol and methyl formate. A thermal reaction of excess methyl acetate with the metal clusters and particles formed upon warmup would account for the formation of methanol and methyl formate; this appears to be a minor reaction pathway in both cases.

An attractive rationalization of the photoformation of acetaldehyde and formaldehyde in this system is illustrated in Scheme I. The formation of adduct 1 has been demonstrated at 15 K by using matrix isolation spectroscopy where cocondensation of chromium and methyl acetate producted clearly discernible shifts in the carbonyl and C–O stretching frequencies.[10] The existence of a stable ligated metal species at 77 K can be shown by the fact that the same products are producted if the reactants are first cocondensated and then the matrix is photolyzed. The extremely high organic to metal ratio required for this reaction clearly indicates that a metal atom reaction is occurring. Photoinsertion of the chromium atom into the C–OCH_3 bond of the adducted ester would form intermediate 2. Decomposition of 2 by β-hydride transfer[11] and reductive elimination[12] would then yield acetaldehyde and formaldehyde in equimolar quantities; the low observed yield of formaldehyde may be accounted for by its difficulty of isolation. Photolytic cocondensation of chromium and methyl acetate-d_3 yields acetaldehyde-d_3 as predicted by this mechanism.

Other acetate esters also react with chromium vapor to yield acetaldehyde, but the efficiency of the reaction drops dramatically as the size of the alkyl group is increased.

We are continuing to investigate the photolytic reactions of metal atoms with other organic compounds, and the results of these studies will be reported later.

Acknowledgment. We gratefully acknowledge the 3M Co. for support of this work.

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(9) Over a 3-h period 0.36 mmol of chromium was condensed with 256 mmol of methyl acetate. Volatile products were identified by GC and GC/MS using a Porapak QS column. The yield of acetaldehyde was determined by using benzene as an internal standard.

(10) Methyl acetate and chromium vapor were codeposited with excess argon onto a copper surface. Stretching frequencies were determined by using a Beckman IR-9 infrared spectrometer. The carbonyl and C–O stretching frequencies of adduct 1 were measured as 1687 and 1110 cm^{-1}, respectively, compared to 1799 and 1252 cm^{-1} for free methyl acetate.

(11) β-Hydride shifts in metal–methoxyl compounds have been observed. Chaudret, B. N.; Cole-Hamilton, D. J.; Nohr, R. S.; Wilkinson, G. *J. Chem. Soc. Dalton Trans.* 1977, 1546.

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Direct Synthesis of Low-Valent Acyl Isocyanide Metal Complexes. Preparation, Structure, and Properties of $(\eta^5\text{-}C_5H_5)Co(CNCOR)_2$ Complexes Formed via Reaction of $(\eta^5\text{-}C_5H_5)Co(CO)_2$ with Acyl Isocyanides

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Summary: Compounds $(\eta^5\text{-}C_5H_5)Co(CNCOR)_2$, R = C_6H_5 (Ia) and 1-adamantyl (Ib), have been prepared, Ia for the first time and Ib in improved yield, by displacement of CO from $(\eta^5\text{-}C_5H_5)Co(CO)_2$ by CNCOR at ambient temperature. This exceptionally easy complete displacement of CO is attributed to the strong π-acceptor character of the acyl isocyanide ligand.

The acyl isocyanide ligand :C≡NC(=O)—R has been shown, by its effect on carbonyl ligand stretching fre-

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quencies and mass spectroscopic ion abundances in mixed-ligand complexes, to more closely resemble CO in its electronic properties than does a simple alkyl or aryl isocyanide. The acyl isocyanide may in fact be a better π-acceptor than CO itself.[1] This electronic similarity between carbonyl and acyl isocyanide ligands has been applied to the synthesis of homogeneous catalysts with chiral metal centers.[2] In that work, as in all previous studies,[3] the acyl isocyanide ligands, which are unstable as uncoordinated molecules, were assembled at the metal center via acylation of cyanometalates. Recently it was reported that a metalloporphyrin acyl isocyanide complex could be prepared by trapping free acyl isocyanide with a reactive, coordinatively unsaturated metal center.[4] We wish to report that free acyl isocyanides are capable of displacing carbonyl ligands from metal carbonyl complexes at a rate which is favorably competitive with the oligomerization of the uncoordinated isocyanides. This has enabled us to prepare the previously reported[5] η^5-$C_5H_5Co[C{\equiv}NC({=}O)R]_2$ complexes in vastly improved yield, as well as providing routes to new acyl isocyanide complexes of other metals.

Benzoyl isocyanide, prepared in acetonitrile solution via the literature procedure,[6] reacts with $CpCo(CO)_2$ (Cp = η^5-C_5H_5) to produce the new compound $CpCo[CNCOPh]_2$ (Ia) in 69% yield.[7] The reaction occurs at room temperature and is accompanied by gas evolution with a variable induction period. This loss of both CO ligands at ambient temperature is exceptional. There are few examples of clean displacement of both CO groups from $CpCo(CO)_2$ by unidentate ligands.[8] The ability of benzoyl isocyanide to totally replace CO is consistent with its greater π-acceptor strength. Characterization of the product follows from its IR and NMR spectra, which are similar to the previously reported[5] R = adamantoyl (Ib) and pivaloyl (Ic) isocyanide analogues, from elemental analysis[9] and from an X-ray diffraction study. The presence of the conjugated phenyl groups in Ia causes a decrease in the ν_{CN} and ν_{CO} IR frequencies relative to Ib and Ic, consistent with increased π-acceptance by the aroyl isocyanide ligand relative to its alkanoyl analogues.

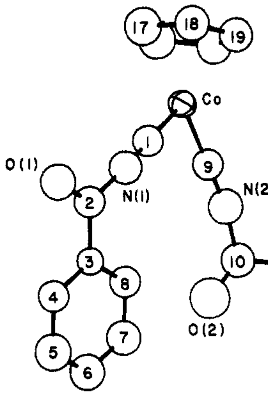

Figure 1. Molecular structure of $(\eta^5\text{-}C_5H_5)Co(CNCOC_6H_5)_2$ showing 50% probability ellipsoid for the Co atom. The Co–C distances are Co–C(1) = 1.704 (13) and Co–C(9) = 1.695 (12) Å.

The molecular structure of Ia, which confirms the structure inferred from IR and NMR spectra, is shown in Figure 1.[10] Although the two acyl isocyanide ligands are not symmetrically disposed, they are otherwise nearly identical. Furthermore, their geometry is very similar to that observed in $(\eta^6\text{-}C_6H_5CO_2CH_3)Cr(CO)_2(CNCOC_6H_5)$,[2a] including the short N···O interactions in the M-CN-CO group (2.26 vs. 2.25 Å in the present case). The C=N—C angles are again far from linear (C(1)–N(1)–C(2) = 164 (1)° and C(9)–N(2)–C(10) = 170 (1)°); the value for the analogous angle in the Cr complex is 168 (1)°.

An analogous synthetic procedure starting with 1-adamantanecarbonyl isocyanide produces Ib in 25% yield, compared to the previous synthesis via acylation of $CpCo(CN)(CO)^-$ in 7% yield. These bis(acyl isocyanides), which are the first examples of low-valent metal complexes containing acyl isocyanide ligands without additional carbonyl ligands, are thus available for further study.

Of particular interest is the opportunity these compounds provide for an *intermolecular* comparison between the electronic capabilities of CO and CNC(=O)R ligands. Unsuccessful efforts to synthesize Co(II) of (III) acyl isocyanide complexes via acylation of $CpCo(CN)_2^-$ and $CpCo(CN)_3^{-}$[5] suggest that the acyl isocyanide ligand is similar to CO not only in its excellent π-acceptor ability but also in being a weak σ-donor best stabilizing low oxidation states. We thus decided to test the chemical analogy between Ia and $CpCo(CO)_2$ by comparing their reactivities in reactions well-known for the latter compound.

Complex Ia and $CpCo(CO)_2$ differ in their electrochemical behavior. Thus, cyclic voltammetry on $CpCo(CO)_2$

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[7] *Caution*: acyl isocyanides and some of their metal complexes are readily hydrolyzed by traces of water to produce HCN. All procedures are carried out under nitrogen with scrupulously dry solvents, either via Schlenk techniques or in a glovebox. A solution of PhC(=O)N≡C, prepared from 5.19 g (22.4 mmol) of PhCOI and 7.0 g (52 mmol) of AgCN in MeCN, is added to a solution of 1.26 g (7.00 mmol) of $CpCo(CO)_2$ in MeCN and allowed to stir until $CpCo(CO)_2$ is consumed (IR) (several hours at ambient temperature). Solvent is removed in vacuo, and the remaining red-brown solid is dissolved in ca. 100 mL of THF. The THF solution is filtered, and the very dark reddish brown filtrate is evaporated to dryness in vacuo. The resultant dark solid is dissolved in 50–60 mL of warm MeCN, and this solution is filtered warm. On cooling to −30 °C, very dark reddish brown or red-black crystals or powder form, which are washed with cold MeCN and dried in vacuo, yield 1.86 g (69%). If necessary, recrystallization from warm MeCN may be repeated. Ia is stable to dry air for extended time periods as a solid, but solutions are quite air-sensitive.

[8] For example, replacement of the second CO by aryl isocyanides requires temperatures ≥ 120°, and is not observed for alkyl isocyanides: Yamamoto, Y.; Mise, T.; Yamazaki, H. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 2743–4.

[9] IR (THF): 2005 (m), 1913 (s), 1687 (sh), 1673 (s) cm^{-1}. ^1H NMR (90 MHz, C_6D_6): δ 8.1 (m, 4 H, Ph), 7.1 (m, 6 H, Ph), 4.73 (s, 5 H, Cp). CIMS (CH_4): m/z [relative intensity] 415 [0.05, $(M + C_2H_5)^+$], 387 [0.7, $(M + H)^+$], 386 [0.5, $(M)^+$], 293 [0.4, $(M - Cp - CO)_+$], 265 [0.5, $(M - Cp - 2CO)^+$], 226 [1.1, $(M - H - CO - CN - COPh)^+$], 105 [100, $(COPh)^+$]. Melting point: 114–115 °C. A sample for elemental analysis was purified by flash chromatography on octadecylsilica using THF eluant. Anal. Calcd for $C_{21}H_{15}N_2O_2Co$ (Found): C, 65.30 (65.37); H, 3.91 (4.15); N, 7.09 (6.97).

[10] Crystal data: space group $C2/c$ (no. 15), monoclinic, a = 13.634 (2) Å, B = 11.665 (2) Å, c = 23.682 (5) Å; β = 108.37 (2)°; V = 3574.5 $Å^3$; Z = 8; fw = 386.30; ρ_{calcd} = 1.44 g cm^{-3}; $\mu_{MoK\bar{\alpha}}$ = 10.2 cm^{-1}. Data were collected to a maximum $2\theta \leq 45°$ (Mo $K\bar{\alpha}$); full matrix least-squares refinement of positional and isotropic thermal parameters for all atoms (using anisotropic thermal parameters for Co) led to R = 0.079 and R_w = 0.089, for 1290 data for which $F > 3.92\sigma(F)$. Total parameters varied in the refinement: 110.

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$_2$Fe$^{0/+}$. 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·HgCl$_2$ appears to be significantly more labile than CpCo(CO)$_2$·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$_5$Me$_5$Rh(CO)$_2$ at ambient temperature and with Mn(CO)$_5$Br 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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(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$_2$O$_2$CoHgCl$_2$ (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$_5$Me$_5$Rh(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)$_n$(μ-SCH$_2$) (n = 10, 11)

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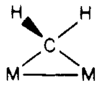
Summary: Reaction of Os$_3$(CO)$_{11}$(μ-CH$_2$) with ethylene sulfide leads to transfer of sulfur to the methylene group in the cluster complex and formation of the new complexes Os$_3$(CO)$_{11}$(μ-SCH$_2$) and Os$_3$(CO)$_{10}$(μ_3-SCH$_2$) which contain doubly and triply bridging thioformaldehyde 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)$_{11}$(μ-CH$_2$) with 50 μL of ethylene sulfide in 15 mL of refluxing cyclohexane

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