Mechanism of the Decarbonylation of $RC(O)CCo_3(CO)_9$ to $RCCo_3(CO)_9$: Migration of the Ketonic Carbonyl

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Received September 17, 1986

Carbynyl tricobalt clusters of the type $ArCOCCo_3(CO)_9$ are known to decarbonylate upon heating to yield the corresponding $ArCCo_3(CO)_9$ systems. The origin of the extruded CO has been determined by specific labeling with ^{13}CO. It is shown by ^{13}C NMR spectroscopy that the initial loss of carbon monoxide occurs at a tricarbonylcobalt vertex and the product arises via migration of the ketonic carbonyl to the vacant coordination site on cobalt. The relevance of these observations to the known carbonylation reactions of carbynyltricobalt nonacarbonyl clusters is discussed.

Introduction

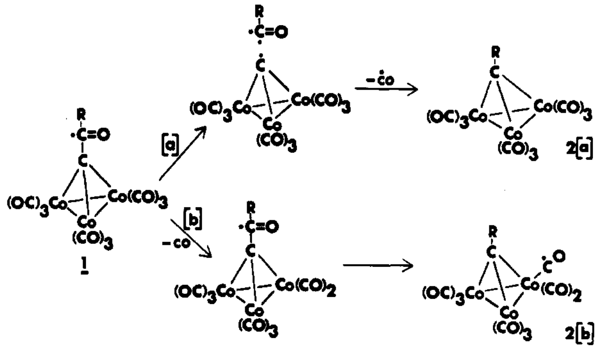
In the course of his pioneering studies on the reactivity of organic derivatives of carbynyltricobalt nonacarbonyl clusters, Seyferth[1,2] observed that acyl derivatives such as 1 could, in some cases, be decarbonylated to give the corresponding alkyl or aryl complexes 2. Various mechanistic possibilities were advanced, e.g., [a] a Norrish-type I photolysis[3,4] route giving rise to radical-coupled products after extrusion of the ketonic CO and [b] loss of a metal carbonyl ligand with concomitant molecular rearrangement, as in Scheme I.

The fact that the decarbonylation occurred on thermolysis, even in the dark, seemed to militate against the Norrish-type radical fragmentation, but, nevertheless, the mechanism remained an open question. It is apparent from Scheme I that one way to distinguish between these pathways would be to isotopically label the ketonic carbonyl group and then locate the labeled CO in the reaction products. To this end, we synthesized the starting material specifically enriched in ^{13}C with a view to monitoring the progress of the reaction by NMR spectroscopy.

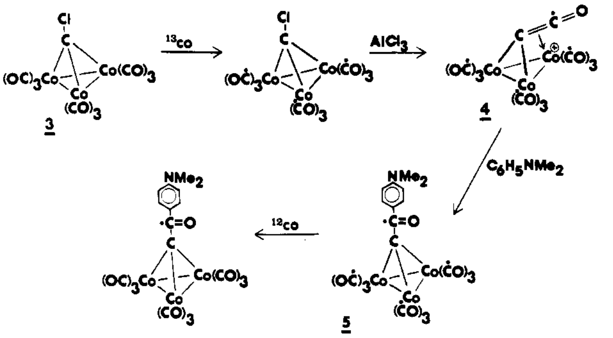
Results and Discussion

In order to differentiate between the mechanistic proposals outlined in Scheme I, it is necessary to label one of the carbonyl environments and then see whether any carbonyl transfer has been effected during the decarbonylation. Thus, if the ketonic position were enriched in ^{13}CO and if pathway [b] were operative, then the decarbonylated product 2[b] would possess one enriched metal carbonyl position and the normally rather weak ^{13}C NMR resonance at approximately 200 ppm would be appropriately enhanced. In contrast, if the ketonic CO were the one eliminated, to yield 2[a], then no such enhancement of the 200 ppm signal would be observed.

Scheme I. Proposed Pathways for Loss of CO from Aroyltricobalt Clusters



Scheme II. Synthetic Route to a Cluster Specifically Labeled at the Ketonic Carbonyl Position[a]



[a] Note: throughout this paper, C* indicates a carbon position enriched in carbon-13 to the extent of about 25–30%.

At first sight it might appear that one should merely synthesize a molecule of the type $RC^*(O)CCl_3$ and prepare the desired cluster via direct reaction with $Co_2(CO)_8$. However, the cost effectiveness of such a scheme is unfavorable since yields are low and much of the carbon-13 label would be wasted. Instead, we chose to use ^{13}CO as the source of our isotopic label and proposed to carry out the synthetic sequence outlined in Scheme II. We have already demonstrated[5] that enrichment of $ClCCo_3(CO)_9$ (3) with ^{13}CO and subsequent treatment with $AlCl_3$ yield the ketenylidene cation 4 labeled not only at the cobalt carbonyls but also at the potentially ketonic site. Addition of a suitable nucleophile, such as *N,N*-dimethylaniline, leads to the Friedel–Crafts product 5 which, in principle, could be "de-enriched" at the metal carbonyl positions by treatment with ^{12}CO. Figure 1 shows the ^{13}C NMR spectrum of 5 showing ca. 25% ^{13}C enrichment for both types of carbonyl environment. However, the exchange of the metal carbonyls in 5 with ^{12}CO turned out to be an exceedingly slow process, and even after numerous expo-

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[1] Seyferth, D.; Nestle, M. O.; Eschbach, C. S. *J. Am. Chem. Soc.* **1976**, *98*, 6724.

[2] Seyferth, D.; Nestle, M. O. *J. Am. Chem. Soc.* **1981**, *103*, 3320.

[3] Balltrop, J. A.; Coyle, J. D. *Excited States in Organic Chemistry*; Wiley: New York, 1975; pp 180–183.

[4] (a) Engel, P. S. *J. Am. Chem. Soc.* **1970**, *92*, 6074. (b) Robbins, W. K.; Eastman, R. H. *J. Am. Chem. Soc.* **1970**, *92*, 6076.

[5] D'Agostino, M. F.; Mlekuz, M.; Kolis, J. W.; Sayer, B. G.; Rodger, C. A.; Halet, J.-F.; Saillard, J.-Y.; McGlinchey, M. J. *Organometallics* **1986**, *5*, 2345.

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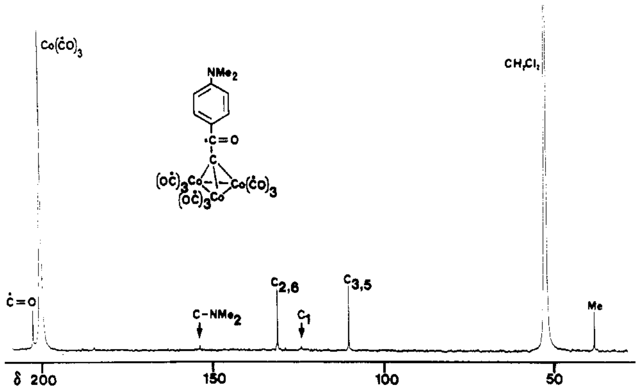
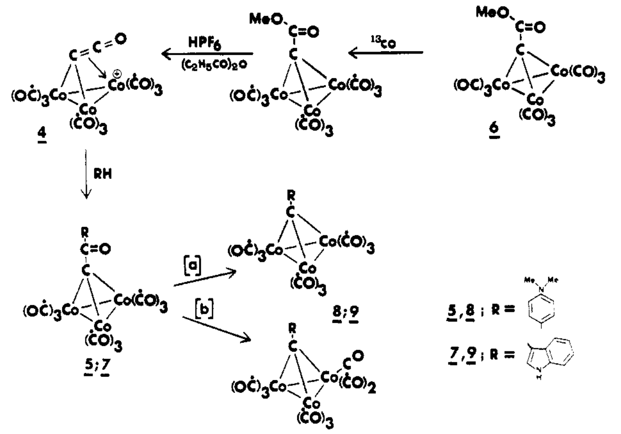


Figure 1. 62.8-MHz ^{13}C NMR spectrum of **5** enriched at all ten carbonyl positions.

Scheme III. Synthetic Route to a Cluster Specifically Labeled at the Cobalt Carbonyl Positions



sures to fresh ^{12}CO over a several month period the ^{13}CO content had scarcely changed.[6] In retrospect, it is clear that the rate of incorporation of ^{13}CO to take a naturally abundant sample to, say, 25% ^{13}C content is much faster than that for the reverse process which takes a 75% ^{12}CO-containing molecule back up to the natural abundance level. In the latter case, 75% of the CO molecules exchanged have no effect and the situation worsens as the reaction proceeds. The kinetics of consecutive reactions have been recently discussed by Atwood.[7] It is, of course, true that CO exchange occurs more rapidly at elevated temperatures, but the thermal instability of **5** precludes such an option.

Having learnt our lesson, we followed the course outlined in Scheme III in which initial ^{13}CO enrichment of the ester **6** and subsequent treatment with HPF_6 in propionic anhydride produced the cation **4** enriched only at the cobalt carbonyls. Reaction of **4** with *N*,*N*-dimethylaniline (or indole) gave good yields of **5** (or **7**) enriched in ^{13}CO only at the cobalt carbonyls while the ketonic carbonyl retained its normal 1% abundance. We are thus labeling the ketonic position with ^{12}CO and looking for a diminution of the ^{13}C isotopic content at the basal carbon positions; this is merely the reverse of the original experiment that envisaged ^{13}C enrichment solely at the ketonic position and then tested for enrichment at the $Co(CO)_3$ sites. Now if the reaction were to follow a mechanism in which the ketonic carbonyl were extruded, such as the Norrish-type proposal, the ratio of the intensity of the metal carbonyl ^{13}C NMR resonance at 200 ppm to the intensities of the other peaks should be essentially unchanged on going from **5** to **8**[a]. In contrast, if a CO ligand bonded to cobalt were to be lost and its position taken by the former ketonic carbonyl, then, in the resulting decarbonylated molecule **8**[b], only eight of the terminal carbonyls will be enriched while the ninth CO ligand would be merely naturally abundant in ^{13}C. The overall result will be a diminution in the intensity of the cobalt carbonyl resonance relative to those of the remainder of the ^{13}C peaks in the spectrum by a factor of 1 in eight or 12.5%. [Note that the actual percentage of ^{13}CO enrichment is unimportant; it is merely the relative change with respect to the remaining ^{13}C nuclei in the molecule which are, of course, naturally abundant.]

Of course, the crucial assumption in this experiment is that the ^{13}C NMR relaxation times and relative sensitivities remain constant for the carbonylated and decarbonylated molecules. It was clearly incumbent upon us to establish whether this assumption is indeed justified and, if not, to correct for it. We had two things to investigate: (a) the reproducibility of a given spectrum and (b) the constancy of the relative relaxation times. To satisfy ourselves as to the first point, we ran each ^{13}C spectrum three times under identical conditions. These spectra were all obtained by using overnight runs on a Bruker AM500 spectrometer operating at 11.7 T (500 MHz for ^{1}H; 125 MHz for ^{13}C) in order to get good signal to noise conditions. Typically, these spectra were the result of ~200 000 transients, and, gratifyingly, the relative integrated intensities of the ^{13}C resonances in separate runs differed by less than ±1%. In each case, the integrated intensity of the cobalt carbonyl resonance was taken as the internal standard and the intensities of the resonances of the indolyl ligand were normalized to this. The internal consistency was, in fact, better than we had anticipated and is presumably a consequence of the very large number of scans and the inherent sensitivity and stability of the high-field instrument.

The second criterion, that is, the relative constancy of the relaxation times of the different ^{13}C sites in the carbonylated and decarbonylated molecules is not so trivial to establish. Clearly, this has to be accomplished on a system uncomplicated by the presence of different isotopic abundances in the ketonic and metal carbonyl positions. On the other hand, the cobalt carbonyls need to be enriched so as to give acceptable signal intensities in a reasonable time period. To achieve this, the indole complex **7** was prepared by using the sequence outlined in Scheme II. By this means, the ketonic carbonyl is enriched to exactly the same extent as are the basal carbonyls since they originate from the same ^{13}C-enriched carbonyl pool, i.e., from the chloro compound **3**. Now, decarbonylation of **7** made in this way gives us no information as to the origin of the CO that is eliminated, but it does provide a standard with which to compare the relative intensities of the cobalt carbonyls and the carbon resonances of the indolyl ligand in both the carbonylated and decarbonylated molecules. Again, we were fortunate to find that the variation of the relative integrated intensities of the carbon resonances of the indolyl ligand in both clusters, normalized to those of the $Co(CO)_3$ signals, was no more than ±1.5% in three overnight runs on the AM500. The sole exception was the C-2 carbon, i.e., the nucleus that suffers the greatest change in its environment going from a position next to a ketonic carbonyl to a site contiguous to the carbynyl carbon. We could thus proceed with some confidence to the experiment in which the molecule enriched

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[6] We find that the rate of ^{13}CO exchange follows the sequence Cl > ester ≫ aroyl; for discussion of carbonyl exchange in such systems, see: Cetini, G.; Ercoli, R.; Gambino, O.; Vaglio, G. *Atti Accad. Sci. Torino, Cl. Sci. Fis., Mat. Nat.* **1964**, *99*, 1123; *Chem. Abstr.* **1968**, *68*, 72774.

[7] Atwood, J. D. *Inorganic and Organometallic Reaction Mechanisms*; Brooks/Cole: Monterey, CA, 1985; pp 7–12.

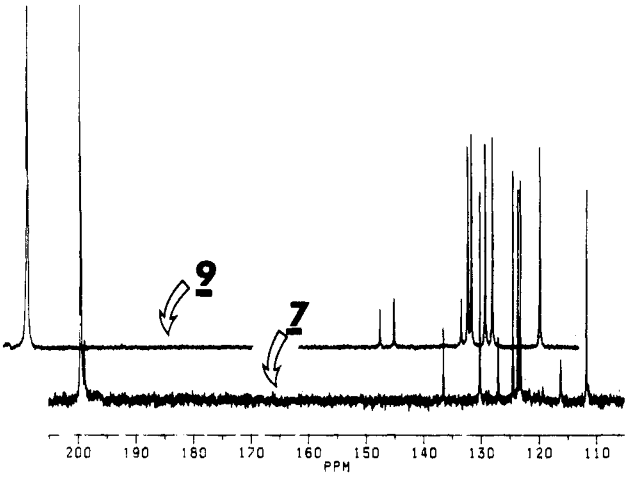
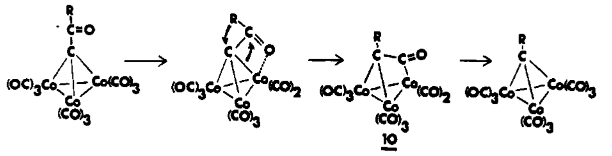


Figure 2. 125.7-MHz ^{13}C NMR spectra of **7** and **9**. Note that the indolyl resonances are the same intensity in both spectra, but the cobalt carbonyl peak is much reduced in the spectrum **9**.

Scheme IV. Proposed Mechanistic Scheme Showing Loss of a Cobalt Carbonyl and Migration of the Ketonic Moiety



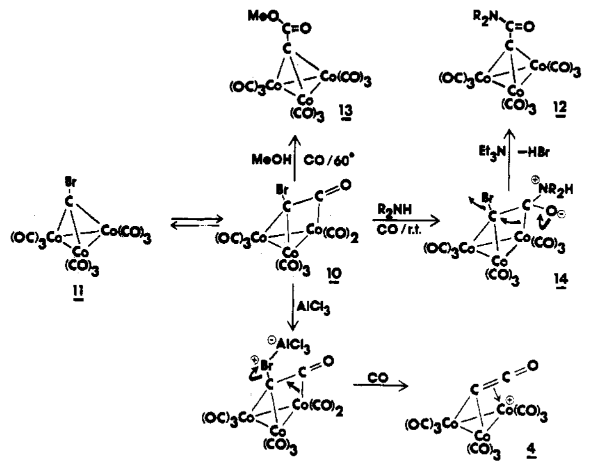
only at the cobalt carbonyl positions was decarbonylated.

In our hands, the cleanest decarbonylation process occurred for **7** → **9**, i.e., when R = 3-indolyl. Figure 2 shows the 125-MHz ^{13}C NMR spectra of the carbonylated and decarbonylated clusters, and it is readily apparent that in going from **7** to **9** the ketonic carbonyl at 198.6 ppm has disappeared. Furthermore, the intensity of the 200 ppm peak in **9** has apparently been reduced with respect to the indolyl ligand resonances. In fact, the measured integrated intensities show that the cobalt carbonyl resonance in **9** has been reduced by 12–14% relative to the other ^{13}C peaks.

We can thus unequivocally deduce that the CO originally lost was a cobalt carbonyl and that its place was taken by the CO moiety from the ketonic position. Before proposing a mechanistic rationale, we note that the rate and extent of decarbonylation are very sensitive to the identity of the acyl fragment. In particular, Seyferth has reported[2] (and we have confirmed) that decarbonylation is favored when the RC=O group contains an electron-releasing substituent; i.e., $p\text{-}Me_2NC_6H_4 > p\text{-}MeC_6H_4 > C_6H_5 > p\text{-}FC_6H_4 > p\text{-}ClC_6H_4$. One might envisage that loss of a cobalt carbonyl is followed by interaction of the acyl group with the vacant coordination site, as in Scheme IV. There must be a developing electron deficiency at the carbynyl carbon atom, and this is alleviated by migration of the R group to this terminus. The aryl functionalities listed above follow the classic pattern of migratory aptitudes expected for migration towards an electron-deficient center such as a carbocation, carbene, or nitrene.[8]

A reviewer has suggested that initial loss of the ketonic CO followed by rapid scrambling of the liberated CO with the carbonyls of the $Co(CO)_3$ groups could account for the decreased intensity of the metal carbonyl ^{13}C NMR resonances. It was pointed out that these tricobalt clusters pick up CO almost quantitatively as in the case of the transformation of the chloro cluster **3** to the acylium ion **4**. We note, however, that the production of **4** from **3** is essentially unaffected by the presence of free carbon monoxide.[14] In that reaction, which proceeds in good yield even at low temperature, the newly created vacant coordination site on cobalt must interact with a bonded CO from another molecule rather than with gaseous carbon monoxide. Furthermore, the experimental data presented here show that, within experimental error, the entire population of ketonic ^{12}CO's is transferred to the basal position; i.e., the $Co(CO)_3$ peak intensity decreases by the expected 12.5% (±1%). It is unrealistic to expect that, if initial extrusion of ^{12}CO from the ketonic position were the predominant mechanistic process, *all* of this ^{12}CO could successfully substitute at the coordinatively saturated $Co(CO)_3$ vertices.

Scheme V. Proposed Mechanistic Scheme for Carbonylation Reactions of Halocarbynyltricobalt Nonacarbonyl Clusters



Finally, it is interesting to speculate about the possibility that some of the individual steps in Scheme IV are reversible. Thus, electron-donating R groups clearly favor migration toward the carbynyl carbon with concomitant molecular rearrangement, presumably to give initially the carbonyl-bridged structure **10**. One could visualize a situation whereby electron-withdrawing groups might promote the reverse process in which carbonyl insertion occurs. It is particularly noteworthy that, when $BrCCo_3(CO)_9$ (**11**) was treated with triethylamine under an atmosphere of CO, infrared absorptions attributable to bridging carbonyls were observed.[9] Furthermore, it is well-established that **11** reacts readily with amines or alcohols to give cluster-bound amides, **12**, and esters, **13**, respectively.[9,10] Likewise, thiols yield thioesters, but subsequent side reactions lead to complications.[11]

A straightforward mechanism that readily accommodates all these observations is outlined in scheme V. If one accepts the existence of a small equilibrium concentration of the carbonyl-bridged isomer **10**, then nucleophilic attack at the ketonic carbonyl leads to the intermediate **14**; elimination of HBr yields directly amides, **12**, or esters, **13**, depending on the identity of the nucleophile. Such reactions are greatly facilitated by the addition of triethylamine whose role is presumably to accelerate the elimination of HBr. It is also easy to see why addition of

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[8] Gould, E. S. *Mechanism and Structure in Organic Chemistry*; Holt, Rinehart, Winston: New York, 1959; pp 609–629.

[9] (a) Seyferth, D.; Nivert, C. L. *J. Organomet. Chem.* **1976**, *113*, C65. (b) Seyferth, D.; Rudie, C. N. *J. Organomet. Chem.* **1980**, *184*, 365. (c) A structure analogous to **10** has been proposed as a possible intermediate during the carbonylation of a C_6H_5C unit coordinated to a cobalt surface: Meyers, G. F.; Hall, M. B. *Organometallics* **1985**, *4*, 1770.

[10] Ercoli, R.; Santambrogio, E.; Tettamante Casagrande, G. *Chim. Ind.* (*Milano*) **1962**, *44*, 1344.

[11] Seyferth, D.; Rudie, C. N.; Merola, J. S.; Berry, D. H. *J. Organomet. Chem.* **1980**, *187*, 91.

a strong Lewis acid, such as aluminum trichloride, favors generation of the ketenylidene cation **4** whose tilted geometry[5] is readily achievable by a very minor distortion from the carbonyl-bridged conformation of **10**. We suggest, therefore, that decarbonylation and carbonylation reactions of the carbynyltricobalt nonacarbonyl clusters proceed via common intermediates and that the direction of the equilibrium is a consequence of the electron-withdrawing or -donating character of the apical group.

To conclude, we have shown that in the decarbonylation of the acyl systems $RC(O)CCo_3(CO)_9$ to give the corresponding $RCCo_3(CO)_9$ clusters, the carbon monoxide which is lost is derived from a tricarbonylcobalt vertex. We are currently studying the kinetics of these reactions and also synthesizing acyl clusters containing a chiral R group to see whether the migration proceeds intramolecularly with retention of configuration.

Experimental Section

All experiments were carried out under an atmosphere of dry nitrogen; solvents were dried and distilled before use.[12] NMR spectra were recorded by using Bruker AM500 and WM250 spectrometers operating at 500 or 250 MHz, respectively, for ^1H and at 125.7 and 62.8 MHz, respectively, for ^{13}C. Carbon-13 spectra were acquired with composite pulse decoupling, a 20° pulse, 0.55-s acquisition time, and digital resolution of 0.9 Hz/pt. On the basis of the consistency of the integrated areas of the indolyl carbons, relaxation was considered sufficiently complete to yield quantitative data. Infrared spectra were obtained on a Perkin-Elmer 283 instrument and mass spectrometry was performed on a VG micromass 7070F spectrometer equipped with a VG 2035 data system; this system incorporates isotopic simulation and deconvolution programs.

Preparation of $ClCCo_3(C^*O)_9$ (3). Following Seyferth's procedure,[13] $Co_2(CO)_8$ and CCl_4 in tetrahydrofuran reacted to give $ClCCo_3(CO)_9$ (**3**) which was exposed to an atmosphere of ^{13}CO. After 48 h, the CO was removed and fresh ^{13}CO was added. Mass spectrometry indicated that the resulting product was enriched at the carbonyl carbons to the extent of 25–30%.

Preparation of $Co_3(C^*O)_9CC^*(O)C_6H_4NMe_2$-*p* (5). As described elsewhere,[5] **3** (enriched at the metal carbonyls) was treated with $AlCl_3$ according to the method of Seyferth[14] to yield the cation $[Co_3(C^*O)_9CC^*O]^+$ (**4**) which was in turn treated with *N*,*N*-dimethylaniline to give $Co_3(C^*O)_9CC^*(O)C_6H_4NMe_2$-*p* (**5**) in 69% yield. ^{13}C NMR (CD_2Cl_2): δ 202.3 (ketonic carbonyl), 199.9 (cobalt carbonyls), 153.7 (C^4-NMe_2), 131.4 ($C^{2,6}$), 126.4 (C^1), 110.9 ($C^{3,5}$), 40.1 (methyls).

Attempted De-enrichment of 5. A solution of **5** in CH_2Cl_2 was repeatedly treated with ^{12}CO over a 3-month period in an attempt to exchange the metal carbonyls. The course of the reaction was monitored by ^{13}C NMR, but it was apparent that even over that time period the loss of ^{13}CO was scarcely detectable and the experiment was terminated.

Preparation of $Co_3(C^*O)_9CC(O)$-3-indolyl (7). With use of the ^{13}CO exchange procedure described above, $Co_3(CO)_9CCO_2Et$[14] was enriched at the cobalt carbonyl positions. Subsequent treatment with HPF_6 in propionic anhydride followed by addition of indole[15] gave a 70% yield of **7** enriched only at the metal carbonyls. IR (CH_2Cl_2): ν_{CO} 2100 (m), 2040 (vs), 2020 (s), 1573 cm^{-1}.[16] ^{13}C NMR ($CDCl_3$): δ 199.3 (cobalt carbonyls), 198.6 (ketonic carbonyl), 136.2 (C^8), 129.9 (C^2), 126.7 (C^9), 124.1 (C^4), 123.3 (C^6), 122.8 (C^5), 115.9 (C^3), 111.4 (C^7).[17]

Preparation of $Co_3(C^*O)_9C$-3-indolyl (9). Following the procedure described by Seyferth and Nestle,[2] 3-indolyl–C(O)C–$Co_3(C^*O)_9$ was dissolved in benzene and heated under reflux to bring about decarbonylation. The progress of the reaction was monitored by TLC, and after 3 h all the starting material had disappeared. The product was purified by chromatography on a silica gel column and recrystallized from CH_2Cl_2/hexane. IR (CH_2Cl_2): ν_{CO} 2100 (m), 2040 (vs), 2020 (s) cm^{-1}. ^1H NMR (CD_2Cl_2): δ 8.49 (br s, NH), 7.75 (d, J = 7.2 Hz, H-4), 7.53 (s, H-2), 7.42 (d, J = 7.5 Hz, H-7), 7.29 (m, H-6), 7.26 (m, H-5). ^{13}C NMR (CD_2Cl_2): δ 200.7 (cobalt carbonyls), 139.5 (C^3), 137.0 (C^8), 125.3 (C^9), 124.2 (C^2), 123.6 (C^6), 121.1 (C^5), 119.9 (C^4), 111.7 (C^7).[18]

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Natural Sciences and Engineering Research Council of Canada for financial support. It is a particular pleasure to thank Dr. M. Mlekuz (University of Ottawa) and Dr. J. W. Kolis (Clemson University) for helpful discussions. M.F.D. was the recipient of an NSERC post-graduate scholarship.

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(12) Perrin, D. D.; Perrin, D. R. *Purification of Laboratory Chemicals*; Pergamon: New York, 1980.

(13) Seyferth, D.; Hallgren, J. E.; Hung, P. L. K. *J. Organomet. Chem.* **1973**, *50*, 265.

(14) Seyferth, D.; Williams, G. H.; Nivert, C. L. *Inorg. Chem.* **1977**, *16*, 756.

(15) Seyferth, D.; Hallgren, J. E.; Eschbach, C. S. *J. Am. Chem. Soc.* **1974**, *96*, 1730.

(16) In clusters heavily enriched in ^{13}CO, the peak at 2020 cm^{-1} exhibits increased intensity and is slightly broadened; also a weak shoulder is observable at 2010 cm^{-1}. Such behavior is in accord with the well-characterized matrix infrared spectra of cobalt carbonyls derived from enriched CO: Hanlan, L.; Huber, H.; Kündig, E. P.; McGarvey, B. R.; Ozin, G. A. *J. Am. Chem. Soc.* **1975**, *97*, 7054.

(17) The indolyl resonances were assigned by analogy to the closely related 3-formylindole: Rosenberg, E.; Williamson, K. L.; Roberts, J. D. *Org. Magn. Reson.* **1976**, *8*, 117.

(18) These assignments were made via the standard two-dimensional ^1H–^1H (COSY) and ^1H–^{13}C shift-correlated techniques: Benn, R.; Günther, H. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 350.