$O)_{11}L$ ($L = P(C_6H_5)_3$ and $P(OCH_3)_3$) are very similar with respect to number of peaks and their relative intensities,[25] thus these complexes are assumed to be isostructural. Additionally, the three trimethyl phosphite ligands in $HFeCo_3(CO)_9[P(OCH_3)_3]_3$ all occupy axial positions, and it is likely that the $Co_4(CO)_9[P(OCH_3)_3]_3$ derivative has an analogous structure. Hence, the stereochemistries of the products afforded by progressive replacement of CO groups in $Co_4(CO)_{12}$ with $P(OCH_3)_3$ (eq 1) can be viewed as successive substitution of an axial CO ligand with the $P(OCH_3)_3$ ligand. However, questions regarding the site of CO loss in metal carbonyl clusters remain a perplexing challenge.

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Registry No. 1, 76985-82-5; **2**, 76985-81-4.

Supplementary Material Available: Lists of the structure factor amplitudes, calculated atomic coordinates for hydrogen atoms, and bond angles and lengths of the phenyl groups in $Co_4(CO)_{11}P(C_6H_5)_3$ (43 pages). Ordering information is given on any current masthead page.

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(25) Axial and equatorial monocarbonyl substitution in $Co_4(CO)_{12}$ would not however be expected to differ greatly in their ν(CO) infrared spectra. In this connection we are currently performing more quantitative studies (including normal coordinate analyses) on a large variety of monosubstituted and more highly substituted derivatives of group 8 tetranuclear clusters in order to definitively assess solution stereochemistries by means of ν(CO) infrared spectroscopy.

Notes

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Studies Using $(n\text{-Bu})_3P{=}O$ as a Carbon Monoxide Labilizing Ligand in the Synthesis of Metal Carbonyl Complexes Highly Enriched in ^{13}CO

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The requisite utilization of metal carbonyls enriched in carbon-13 has been demonstrated in many investigations. An enumeration of some of these studies would include the following: (1) the determination of intra- and intermolecular CO exchange processes in metal carbonyl mononuclear and cluster species,[1-8] (2) the specification of the site of ligand dissociation and the nature of the resultant intermediate in ligand displacement reactions in solution,[9-12] (3) the identification of metal carbonyl fragments isolated in low-temperature matrices by means of vibrational spectroscopy,[13-15] and (4) the confirmation of the origin of products afforded by catalytic reduction of CO.[16,17]

In all of the processes described above, with the exception of (2) where stereoselective labeling is necessary, the availability of highly ^{13}C-enriched metal carbonyl complexes is generally desirable. Although a few metal carbonyls undergo exchange reactions with free ^{13}CO under mild conditions (e.g., $Ni(CO)_4$ and $Rh_4(CO)_{12}$), most undergo this ligand exchange process reluctantly. Hence straightforward synthetic techniques for the preparation of a large variety of parent metal carbonyl complexes highly enriched in ^{13}CO are imperative. We have briefly reported the preparation of iron pentacarbonyl and the group 6B hexacarbonyls extensively enriched in carbon-13, taking advantage of the CO-labilizing ability of $(n\text{-Bu})_3P{=}O$.[18] As part of an ongoing program to develop the methodology for the syntheses of ^{13}C-labeled metal carbonyl complexes and their derivatives, the scope of the use of $(n\text{-Bu})_3P{=}O$ as a CO-labilizer has been extended, and the results of this investigation are reported herein.

Experimental Section

Materials. $(n\text{-Bu})_3P{=}O$, $Me_3P{=}O$, and $Me_3NO\cdot 2H_2O$ were used as obtained from Apache Chemical Co., Strem Chemical Co., and Aldrich Chemical Co., respectively. Except for $Fe(CO)_5$ (Alfa-Ventron, distilled under N_2 prior to use), all binary metal carbonyls as well as (butadiene)$Fe(CO)_3$ were purchased from Strem Chemical Co. and used without further purification. The substituted metal carbonyl complexes $Cr(CO)_3(NH_3)_3$,[19] $Mo(CO)_4[P(OMe)_3][NHC_5H_{10}]$,[20] $pyFe(CO)_4$,[21] $(pip)_2W(CO)_4$,[22] $(CHT)Cr(CO)_3$,[23] and $K^+(\mu\text{-H})[Cr(CO)_5]_2^-$[24] were prepared in these laboratories by the literature procedures. Carbon-13-enriched CO (93.3% ^{13}CO) was obtained from Prochem., B.O.C., Ltd., Longon, England. The hexane solvent commonly used in the ^{13}CO-exchange reactions was purified by stirring over H_2SO_4/HNO_3, was then washed with water, and finally was distilled from $LiAlH_4$ under N_2. Benzene was distilled under N_2 from sodium wire. Reagent grade octane was not further purified.

Reactions. Schlenk flasks were charged with $(n\text{-Bu})_3P{=}O$ in an argon-filled glovebox. Other manipulations were done under nitrogen by using standard Schlenk techniques.

Reaction of $(H_3N)_3Cr(CO)_3$ with ^{13}CO. The reactions of amine-substituted group 6B metal carbonyl derivatives, $M(CO)_{6-n}(amine)_n$ (n = 1–3, and amine = ammonia, piperidine (pip), or pyridine (py)), and ^{13}CO in the presence of excess $(n\text{-Bu})_3P{=}O$ were all performed in a similar manner. In a typical reaction triamminechromium tricarbonyl (0.272 g, 1.45 mmol, solubility limit) was placed in a 500-mL

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flask containing 165 mL of hexane and 3.01 g (13.8 mmol) of $(n\text{-Bu})_3P{=}O$. The mixture was frozen at −196 °C, degassed, and brought to 1 atm with ^{13}CO. After the septum-sealed flask was warmed in a 70 °C oil bath for 21 h, any solid residues were filtered and the solution was further cooled to −196 °C. Two traps, at −20 and −78 °C, were connected in sequence to the flask containing the frozen reaction solution, which, under dynamic vacuum, was allowed to come to room temperature very slowly by standing in the empty −196 °C Dewar flask. The $Cr(^{13}CO)_6$ sublimed into the −20 °C trap, hexane condensed into the −78 °C trap, and further sublimation of $Cr(CO)_6$ continued. After 1 h, 20 mL of EtOH was added to the solid residues in the reaction flask, dissolving the $(n\text{-Bu})_3P{=}O$ and allowing isolation of more $Cr(CO)_6$. Total recovery of $Cr(^{13}CO)_6$: 0.20 g, 62%.

Reaction of $pyFe(CO)_4$ with ^{13}CO. A 50-mL Schlenk flask, fitted with stirring bar and rubber septum and wrapped in aluminum foil, was charged with $pyFe(CO)_5$ (0.0319 g, 0.137 mmol), $(n\text{-Bu})_3P{=}O$ (0.06 g, 0.275 mmol), and 20 mL of hexane. The solution was frozen, degassed, filled with ^{13}CO, and then placed in a 50 °C bath for 4 h. Vacuum transfer of the volatiles into a −78 °C trap resulted in a hexane solution of carbon-13-enriched $Fe(CO)_5$.

Reaction of $Mn_2(CO)_{10}$ with ^{13}CO. A 100-mL Schlenk flask was charged with $Mn_2(CO)_{10}$ (0.105 g, 0.269 mmol), $(n\text{-Bu})_3P{=}O$ (0.80 g, 3.67 mmol), and 40 mL of hexane. Degassing was followed by back-filling with ^{13}CO and warming to 70 °C for 24 h. Vacuum distillation of the hexane followed by sublimation at 30–35 °C yielded a crude product, which upon resublimation led to recovery of 0.0614 g (0.158 mmol) of enriched $Mn_2(CO)_{10}$, i.e., 59% yield.

Reaction of $Co_4(CO)_{12}$ with ^{13}CO To Yield ^{13}C-Enriched $Co_4(CO)_{12}$. A 50-mL Schlenk flask was charged with $Co_4(CO)_{12}$ (0.0515 g, 0.090 mmol) and $(n\text{-Bu})_3P{=}O$ (0.018 g, 0.0826 mmol), evacuated, back-filled with ^{13}CO, and cooled to −78 °C. After addition of 10 mL of hexane the mixture was warmed to 0 °C and stirred for 18 h. A slight blue ring of side product was observed on the wall of the flask. New $\nu(CO)$ IR bands were observed, ascribable to $Co_4(CO)_{12-n}[^{13}CO]_n$ species. A 35% recovery of $Co_4(CO)_{12}$, enriched in ^{13}C to an estimated level of >75%, was obtained.

Reaction of $Co_4(CO)_{12}$ with Excess $(n\text{-Bu})_3P{=}O$ and $Me_3P{=}O$. A solid-phase reaction was observed on charging a 50-mL flask with 0.054 mmol of $Co_4(CO)_{12}$ and 1.28 mmol of $(n\text{-Bu})_3P{=}O$. Addition of hexane at room temperature resulted in a very rapid reaction with separation of a blue oil from the solvent. The blue oil is soluble in THF and decomposes at 90° C. Visible spectrum: 628, 645, 703 nm. IR (smear): 2960–2860 (C–H), 1910–1850 (very broad, CO), 1156 cm^{-1} (P=O). Identical results were obtained by using $Co_2(CO)_8$ as starting material.

A similar reaction using excess $Me_3P{=}O$ and THF solvent resulted in a purple solution ($\nu(CO)$ = 1890 cm^{-1}), which on addition of hexane produced lavender crystals. Recrystallization from THF/hexane yielded 64% $[((H_3C)_3P{=}O)_6Co][Co(CO)_4]_2$. Anal. Calcd: C, 32.75; H, 5.67; P, 19.52; O, 23.51; Co, 18.55. Found: C, 32.43, 32.67; H, 5.91, 6.08; P, 16.33; O, 27.52; Co, 17.8.

Reaction of $K^+(\mu\text{-H})[Cr(CO)_5]_2^-$ with ^{13}CO in the Presence of H^+ and $(n\text{-Bu})_3P{=}O$. A 22-fold molar excess of $(n\text{-Bu})_3P{=}O$ was added to 0.025 mmol of $K^+(\mu\text{-H})[Cr(CO)_5]_2^-$ in a 50-mL Schlenk flask. Two milliliters of THF was added and the resulting solution degassed, back-filled with ^{13}CO, and acidified with 7 mL of 0.1 M anhydrous HCl/THF solution. The reaction mixture was allowed to stir at 50 °C for 15 h and cooled, and THF was removed under vacuum. A hexane solution infrared spectrum of the residue indicated the presence of $Cr(^{13}CO)_6$ enriched to >90%.

Reaction of $Cr(CO)_6$ with Me_3NO and ^{13}CO in the Presence of $(n\text{-Bu})_3P{=}O$. In a typical experiment a 50-mL Schlenk flask, fitted with stirring bar and rubber septum cap, was charged with $Cr(CO)_6$ (0.013 g, 0.06 mmol), Me_3NO (0.040 g, 0.357 mmol), $(n\text{-Bu})_3P{=}O$ (0.28 g, 1.28 mmol), and 20 mL of hexane. The flask was twice degassed via freeze–thaw methods and back-filled with ^{13}CO to a pressure of 1.5 atm at 20 °C. The stirred solution was warmed to 70 °C for 15 h, at which time infrared samples were taken. Continued heating showed no further reaction. For the reactant and promoter ratios given here, IR showed $\nu(CO)$ for $Cr(^{12}CO)_6$ (1989 cm^{-1}) and $Cr(^{13}CO)_6$ (1941 cm^{-1}) only, at a band intensity ratio of 20:92, respectively. From a Beers law plot of $Cr(CO)_6$, a total of 35% of $Cr(CO)_6$ was calculated to have survived the reactions. Runs at other Me_3NO concentrations were similarly carried out.

Instrumentation and Analyses. IR spectra were taken in sealed, matched solution NaCl cells on either a Perkin-Elmer 283B or 521 spectrophotometer. Carbon-13 NMR spectra were obtained on a JEOL FX60 spectrometer. Gas chromatographic detection of CO/CO_2 was carried out on a Perkin-Elmer Sigma 2 instrument using a 6 ft × 0.025 in. stainless steel column packed with 80/100 mesh Carbosphere (Alltech Associates). Mass spectral measurements were kindly provided by Professor R. Davis (Kingston Polytechnic, Kingston Great Britain). Elemental analyses were by Galbraith Laboratories.

Results and Discussion

Attempts to extend the scope of the ^{13}CO-exchange reaction as promoted by $(n\text{-Bu})_3P{=}O$ included use of binary metal carbonyl complexes as well as complexes containing a labile ligand. The following metal carbonyl complexes did *not* undergo ^{13}CO exchange at atmospheric pressure and mild temperature either in the absence or in the presence of excess (~10-fold) $(n\text{-Bu})_3P{=}O$ (solvent, temperature of oil bath, and time given in parentheses): $M(CO)_6$ (M = Cr, Mo, W; hexane, 70 °C, 48 h), (butadiene)$Fe(CO)_3$ (octane, 110 °C, 18 h), $Ir_4(CO)_{12}$ (benzene, 80 °C, 20 h). As reported earlier,[18] the following metal carbonyls containing labile ligands underwent multiple-site ^{13}CO exchange in the presence of $(n\text{-Bu})_3P{=}O$, yielding highly enriched $M(^{13}CO)_x(^{12}CO)_y$ compounds: (cycloheptatriene)$Cr(CO)_3$, $pyCr(CO)_5$, $pipMo(CO)_5$, $(py)_3Mo(CO)_3$, $pyFe(CO)_4$, and the tungsten derivatives $pipW(CO)_5$ and $(pip)_2W(CO)_4$ to a lesser extent. In addition we have found that $(n\text{-Bu})_3P{=}O$ effectively enhanced ^{13}CO substitution in $Mn_2(CO)_{10}$, $(H_3N)_3Cr(CO)_3$, and $Co_4(CO)_{12}$. Yield optimization was effected for the first two compounds. The last compound, as well as $Co_2(CO)_8$, underwent the well-known base-assisted valence-disproportionation reaction in excess $(n\text{-Bu})_3P{=}O$ at ambient temperatures. These latter experiments are described below.

Whereas vacuum transfer of volatiles (hydrocarbon solvent plus $M(^{13}CO)_6$ (M = Cr, Mo, W) or $Fe(^{13}CO)_5$) afforded solutions with good to excellent spectroscopic yields of highly ^{13}C-enriched metal carbonyls, isolation of the metal carbonyl free of solvent and phosphine oxide presented experimental difficulties. Since many reactions requiring enriched carbonyls may be run in hydrocarbon or a mixed-solvent system, it is possible that the simple procedure of vacuum transferring volatiles away from the phosphine oxide will yield solutions of enriched metal carbonyls sufficiently pure, and therefore useful as is, for further reactions. We have however endeavored to optimize conditions which would allow for a good isolated yield of $Cr(^{13}CO)_6$ and $Mn_2(^{13}CO)_n(^{12}CO)_{10-n}$. (NB: The formulas used above are expected to convey that in the case of $Cr(CO)_6$, the predominant species obtained is the *all*-labeled $Cr(^{13}CO)_6$, whereas in the case of $Mn_2(CO)_{10}$, the predominant species of highest ^{13}CO incorporation is considerably less than $Mn_2(^{13}CO)_{10}$, where a statistical mixture of 50% ^{13}C-enriched species exists.)

The triammine complex $(H_3N)_3Cr(CO)_3$ was selected for isolated yield optimization since it is an inexpensive, easy-to-prepare labile ligand complex. However its low solubility in the hexane solvent used was most likely a contributing factor to the less than desirable (62%) isolated yield of $Cr(^{13}CO)_6$ obtained. Separation of volatiles was effected by dynamic vacuum successive trapping, with $Cr(^{13}CO)_6$ transferring into the first, −20 °C, trap and hexane going into the next, −78 °C, trap. The level of enrichment was determined to be 90% by ^{13}C NMR and $\nu(CO)$ infrared spectroscopy.[18]

Although $Mn_2(CO)_{10}$ does not undergo CO exchange in the absence of tributylphosphine oxide even at 85 °C, in its presence exchange occurs at 70 °C. Optimization of the level of ^{13}CO incorporation was obtained at a phosphine oxide: $Mn_2(CO)_{10}$ ratio of 13:1, with 30:1 and 5:1 giving substantially lower yields. Manganese decacarbonyl is sufficiently nonvolatile to allow for vacuum removal of solvent, after which pure $Mn_2(CO)_{10}$ could be recovered by sublimation in ca. 60% yield. Mass spectral analysis indicated a 50% enrichment in car-

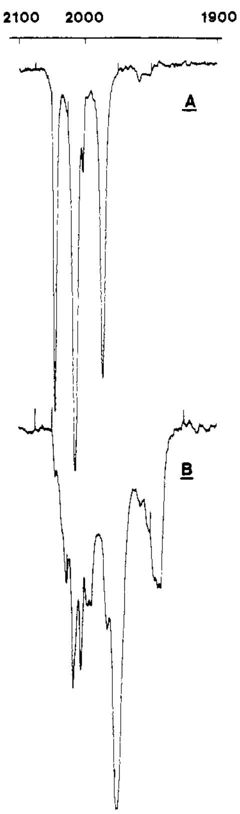

Figure 1. Infrared spectra in the ν(CO) region of $Mn_2(CO)_{10}$ in heptane: (A) natural-abundance ^{13}CO sample; (B) ^{13}CO-enriched sample (50% ^{13}CO by mass spectral analysis).

bon-13. The infrared spectrum in the ν(CO) region is depicted in Figure 1.

As illustrated by the $Mn_2(CO)_{10}$ example, processes other than dissociative ligand loss may generate the open site on the metal believed to be prerequisite for the phosphine oxide labilization. Protonation of the bridging hydride complex $K^+(\mu\text{-}H)[Cr(CO)_5]_2^-$ in the presence of $(n\text{-}Bu)_3P{=}O$ and ^{13}CO gave excellent spectroscopic yields of $Cr(^{13}CO)_6$ with concomitant formation of 1 mol of H_2. In the control experiment, i.e., in the absence of $(n\text{-}Bu)_3P{=}O$, only monolabeled $Cr(^{13}CO)(^{12}CO)_5$ was produced.

In a hypothetically satisfying but experientially less useful approach, the utility of $Me_3N{\rightarrow}O$ toward the oxidative elimination of CO_2 from metal carbonyls[25] was combined with the ligand-labilization properties of $(n\text{-}Bu_3)P{=}O$ in order to effect a "one pot" synthesis of enriched metal carbonyls. Unfortunately the good oxidizing ability of Me_3NO thwarts the utility of this idea. The yields of recovered $Cr(CO)_6$ were consistently small, 14–25% for Me_3NO to Cr mole ratios of 1–6, respectively. Higher ratios converted all of the hexacarbonyl into green, oxidized chromium compounds. Nevertheless, the ^{13}C-labeled $Cr(CO)_6$ at the lower Me_3NO concentrations and a 20-fold excess of $(n\text{-}Bu)_3P{=}O$ showed a quite high level of enrichment, with the all-labeled $Cr(^{13}CO)_6$ being produced at ca. 75% of all species present. In the absence of $(n\text{-}Bu)_3P{=}O$, only $Cr(CO)_6$ and $Cr(CO)_5(^{13}CO)$ were recovered.

It has become apparent that the presence of metal–oxygen bonds in low-valent metal carbonyls greatly facilitates dissociative loss of carbon monoxide, much akin to (but to an even greater extent) that displayed by other hard bases such as Cl^-.[26] For example, in addition to our results utilizing phosphine oxides, $[M(CO)_5O_2CCH_3][PPN]$ (M = Cr, Mo, W) derivatives have been shown to undergo rapid exchange of CO ligands with free ^{13}CO in solution at room temperature.[27,28] The source of the lability of CO groups in these derivatives does not appear to be a function of destabilization of the M–C bonds in the ground-state molecules, for M–C bond distances in these complexes are quite normal (see Table I).[29–37] However, as has been pointed out by Atwood and Brown in other instances,[26] complexes showing extremely labile CO groups also exhibit significant trans M–C bond shortening. Other instances of catalysis of CO substitution or exchange (by both acids and bases) have been discussed in the literature.[38–40]

Table I. Comparative Metal–Carbon Bond Distances in $M(CO)_5L$ Derivatives

M	L	$M{-}CO_{eq}$,[a] Å	$M{-}CO_{ax}$, Å	ref
Cr	CO	1.909 (3)	1.909 (3)	29
Cr	$P(C_6H_5)_3$	1.880 (4)	1.844 (4)	30
Cr	$O_2CCF_3^-$	1.896 (7)	1.815 (7)	27
Cr	$SP(CH_3)_3$	1.900 (4)	1.815 (8)	31
Mo	CO	2.06 (2)	2.06 (2)	32
Mo	$P(C_6H_5)_3$	2.046 (4)	1.995 (3)	33
Mo	$O_2CCH_3^-$	2.05 (1)	1.96 (1)	27
W	CO	2.059 (8)	2.059 (8)	34
W	$P(CH_3)_3$	2.01 (1)	1.98 (1)	35
W	$O_2CCH_3^-$	2.040 (7)	1.952 (7)	36
W	$OP(C_6H_5)_2CHP(C_6H_5)_3$	2.025 (6)	1.949 (10)	37

[a] The average equatorial M–C bond length.

Hence the oxygen-donor ligands' CO-labilizing property has to be due to their effect on the energy of the transition state, a phenomenon which may be explained by using the site preference model.[26] We have thus far not been able to determine whether there is any specificity of CO ligand dissociation in the phosphine oxide intermediate; however, ^{13}CO exchange in $W(CO)_5O_2CCH_3^-$ has been unequivocally demonstrated to occur stereoselectively at cis carbonyl sites.[28]

The reaction of $Co_4(CO)_{12}$ or $Co_2(CO)_8$ with $(n\text{-}Bu)_3P{=}O$ results in disproportionation of the cobalt carbonyls, affording the highly colored $[((n\text{-}Bu)_3P{=}O)_4Co][Co(CO)_4]_2$ salt. At ambient temperature the reaction is immediate, even with stoichiometric amounts of phosphine oxide. This disproportionation process is a well-known reaction of cobalt carbonyls in the presence of a variety of nitrogen and oxygen donor bases, e.g., amines, amino ethers, formamides,[41] and, especially significant to our work, HMPA.[42] The products of these reactions are either four- or six-coordinate cobalt(II) species, $[(base)_nCo][Co(CO)_4]_2$ (n = 4 or 6), depending on the steric requirements of the base. On the other hand, reactions of $Co_2(CO)_8$ with phosphine ligands provide cobalt(I) species of

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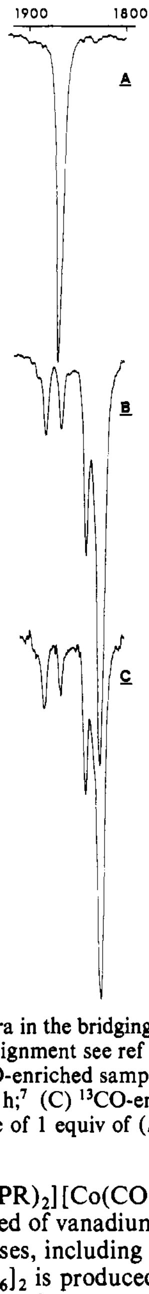

Figure 2. Infrared spectra in the bridging ν(CO) region of Co$_4$(CO)$_{12}$ in heptane (for peak assignment see ref 7): (A) natural-abundance ^{13}CO sample; (B) ^{13}CO-enriched sample (>75%) for exchange reaction at 24.6 °C for 90 h;[7] (C) ^{13}CO-enriched sample for exchange reaction in the presence of 1 equiv of (n-Bu)$_3$P=O at 0 °C for 18 h.

the form [Co(CO)$_3$(PR)$_2$][Co(CO)$_4$].[43] Similar reactions have also been reported of vanadium carbonyls with nitrogen and oxygen donor bases, including (C$_6$H$_5$)$_3$P=O where [V(Ph$_3$P=O)$_4$][V(CO)$_6$]$_2$ is produced.[44] We have isolated a lavender, crystalline salt from the reaction of Co$_4$(CO)$_{12}$ with (CH$_3$)$_3$P=O (the product of the analogous reaction with (n-Bu)$_3$P=O provided a blue oil), which is best formulated as [((CH$_3$)$_3$P=O)$_6$Co][Co(CO)$_4$]$_2$ on the basis of total elemental analyses and infrared spectroscopy (ν(CO) 1980 cm^{-1}, ν(P=O) 1156 cm^{-1}).[45–47] A complete characterization of this species by X-ray crystallographic analysis is planned.

It was nonetheless possible to observe (n-Bu)$_3$P=O-induced CO labilization by carrying out the reaction of Co$_4$(CO)$_{12}$ with 1 equiv of (n-Bu)$_3$P=O in a ^{13}CO atmosphere at 0 °C. Under these conditions ^{13}CO uptake into the cluster was substantial (a control experiment in the absence of (n-Bu)$_3$P=O showed little, if any, ^{13}CO incorporation). Within 18 h a level of ^{13}CO enrichment in Co$_4$(CO)$_{12}$ similar to that requiring 90 h via thermolysis at 24.6 °C in the absence of (n-Bu)$_3$P=O[7] was observed (see Figure 2). Because of the mild conditions under which ^{13}CO exchange occurs in Co$_4$(CO)$_{12}$ in the presence of (n-Bu)$_3$P=O it is highly likely that a radical chain pathway is operative in this instance.[43] Analogous reactions employing the substitutionally more inert Ir$_4$(CO)$_{12}$ cluster, however under much more rigorous conditions (80 °C for 20 h), were unsuccessful at providing ^{13}CO-enriched species. Similarly, whereas Mn$_2$(CO)$_{10}$ readily incorporated ^{13}CO in the presence of (n-Bu)$_3$P=O, Re$_2$(CO)$_{10}$ did not.

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Registry No. (n-Bu)$_3$P=O, 814-29-9; (H$_3$N)$_3$Cr(CO)$_3$, 14974-11-9; Mn$_2$(CO)$_{10}$, 10170-69-1; Co$_4$(CO)$_{12}$, 17786-31-1; pyFe(CO)$_4$, 53317-88-7; K$^+$(μ-H)[Cr(CO)$_5$]$_2^-$, 61453-56-3; Cr(CO)$_6$, 13007-92-6; Co$_2$(CO)$_8$, 10210-68-1; ^{13}CO, 1641-69-6; Me$_3$NO, 1184-78-7; Cr(^{13}CO)$_6$, 25941-09-7; [((n-Bu)$_3$P=O)$_4$Co][Co(CO)$_4$]$_2$, 76721-78-3; [((H$_3$C)$_3$P=O)$_6$Co][Co(CO)$_4$]$_2$, 76721-80-7.

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(47) The ν(P=O) band in [(HMPA)$_4$Co][Co(CO)$_4$]$_2$ occurs at 1188 cm^{-1}.[42]

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Redox Behavior of the [Rh$_2$(1,3-diisocyanopropane)$_4$]$_2^{6+}$ Ion at the Rotating Glassy Carbon Electrode

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During the last several years the chemistry of the family of Rh$_2$(bridge)$_4^{n+}$ (bridge = 1,3-diisocyanopropane, n = 2,3,4) ions has been an area of intense interest to us.[2–11] The initial synthesis of Rh$_2$(bridge)$_4^{2+}$ [2a] led to subsequent studies of the structural chemistry[2b–4] and the photochemistry[4–9] of these ions. Recently, the structure of the [Rh$_2$(bridge)$_4$]$_2$Cl^{5+} ion, which is implicated in the visible-light production of hydrogen from aqueous acid solutions, has been determined.[10] The rich redox chemistry, as well as the need for a further understanding of the thermodynamics of the reactions of the [Rh$_2$(bridge)$_4$]$_2^{6+}$ ion, has prompted us to examine the electrochemical behavior of this ion in acidic aqueous media. The limited solubility and the highly surface-active nature of some oxidation states of the ion (vide infra) were a hindrance in obtaining reproducible cyclic voltammetric data at stationary electrodes. However, a rotating electrode has several advantages over a stationary electrode. It provides a larger steady-state current proportional to the square root of the rotation velocity for species that undergo mass transport and currents independent of rotation velocity for surface species. It can also provide information about the electron-transfer kinetics of a redox system.[12] Herein we report the results of both the oxidation and reduction of the [Rh$_2$(bridge)$_4$]$_2^{6+}$ ion in acidic media at a rotating glassy carbon disk electrode.

Experimental Section

Materials. Rh$_2$(bridge)$_4$(BF$_4$)$_2$ was prepared by a standard method.[2a,4] All reagents were analytical grade. Solutions 0.5 mM in [Rh$_2$(bridge)$_4$]$_2^{6+}$ were made up by weighing a proper amount of Rh$_2$(bridge)$_4$(BF$_4$)$_2$ into a volumetric flask, adding the correct amount of concentrated sulfuric or methanesulfonic acid, and diluting to volume with quadruply distilled water. Air oxidation of Rh$_2$(bridge)$_4^{2+}$ to

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