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Preliminary communication

Sensitized photoreduction of cobalt(II) and iron(II). Structural characterization of $[Co(CO)(o\text{-}C_6H_4[PPh_2]_2)_2]PF_6$

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Abstract

Triplet-state ketones readily sensitized the photoreduction of bis(acetylacetonato)cobalt(II) or Co_{solv}^{2+} under atmospheric pressure of carbon monoxide to give $Co(CO)_4^-$. The low-valent cobalt could be trapped and isolated as phosphine-substituted metal carbonyl complexes. The crystal structure of one of the products, $[Co(CO)(o\text{-}C_6H_4[PPh_2]_2)_2]PF_6$ has been determined. It is orthorhombic, space group *Pbca*, $Z = 8$, with unit cell dimensions a 19.704(5), b 24.850(13), c 21.865(9) Å. Phosphine-substituted iron(0) carbonyl complexes have also been isolated from similar photoreductions of iron(II) species.

Triplet-state benzophenone has been reported to sensitize the photoreduction of $M(acac)_2$ ($M = Cu$ or Ni; acac = acetylacetonate) [1,2] to produce the metastable monovalent acetylacetonate. We have now found that similar sensitized photoreductions of $Co(acac)_2$ also occur readily. In a typical reaction, a combination of MeOH/acetone (with a volume ratio of 4/1) containing 3 mM of Co^{II} was irradiated with a medium pressure Canrad–Hanovia 450-W mercury-vapor lamp through a Pyrex filter (the reaction vessel) under atmospheric pressure of CO. The progress of the reaction was followed by monitoring the IR spectra in the CO stretching frequency region. The photolysis was stopped when ν(CO) of the product reached maximum intensity. $[(Ph_3P)_2N][Co(CO)_4]$ was isolated in 20% yield ***. We found that both a sensitizer (in this case, acetone) and a hydrogen-atom donor (MeOH) were needed for the reduction. For example, no $Co(CO)_4^-$ formed at all if either MeOH or acetone was excluded from the system. A more efficient combina-

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*** After 18 h of photolysis, the solution was transferred to a flask containing one equivalent of $(Ph_3P)_2N^+ Cl^-$ and the solution was stirred for 12 h. Removal of the solvent and recrystallization from $MeOH/H_2O$ gave white crystals of $[(Ph_3P)_2N][Co(CO)_4]$.

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tion of hydrogen atom donor and sensitizer is THF/xanthone (the reduction time is about 1.5 h), possibly due to the much higher extinction coefficient of xanthone than that of acetone in the UV absorption. The efficiency of xanthone is evident from the facile production of $Co(CO)_4^-$ from the photolysis (1.5 h) of $Co(acac)_2$/toluene/xanthone/CO in spite of the extremely low solubility of $Co(acac)_2$ in toluene. We also found that the solvated $Co_{solv}{}^{2+}$ are reduced at a faster rate, i.e., $Co(OAc)_2$ in MeOH/acetone took only about 4 h. Conversion of Co^{2+} to $Co(CO)_4^-$ also takes place under photolytic conditions during the catalytic hydroformylation of olefins [3], and during the conversion of aryl halides to carboxylic acids [4], although the mechanisms of these reactions is uncertain.

It is not certain whether $Co(CO)_4^-$ comes from the disproportionation of $Co_2(CO)_8$ in the solvents [5], but $Co(CO)_4^-$ is the only detectable carbonyl-containing species in the solution. With suitable ligands coexistent in the solution, cobalt(0) or cobalt(I) could be trapped to form substituted metal carbonyls. The presence of diphenylacetylene or triphenylphosphine, induced a very low yield of $Co_2(CO)_6(\mu\text{-}PhC{\equiv}CPh)$ [6] or $Co_2(CO)_6(PPh_3)_2$ [7], in contrast to the major product, $Co(CO)_4^-$. The complexes $Co(CO)_3(PBu_3)_2^+$ [7], $Co(CO)_2(PEt_3)_3^+/Co(CO)_3(PEt_3)_2^+$ [8], $Co(CO)(dppm)_2^+$ [9], $Co(CO)(dppe)_2^+$ [9], and $Co(CO)(o\text{-}C_6H_4[PPh_2]_2)_2^+$ were isolated in low to moderate yields only when appropriate phosphine ligands were used in the reaction *. They were characterized by the IR, ^1H and ^{31}P NMR spectra, and elemental analysis (Table 1). The PF_6 salt of $Co(CO)(o\text{-}C_6H_4[PPh_2]_2)_2^+$ was also structurally characterized by X-ray diffraction (vide infra). We were not able to separate $Co(CO)_3(PEt_3)_2^+$ from $Co(CO)_2(PEt_3)_3^+$, their relative yield depended upon the amount of PEt_3 used. A second product which could not be isolated as a pure compound was identified as $Co_2(CO)_4(dppe)_3^{2+}$ [10] in the reaction with dppe. Rigo [8] reported that Co^{2+} reacted with some unidentate phosphine ligand and CO yielding substituted Co carbonyls, $Co(CO)_xL_{5-x}^+$ (L = phosphines). The degree of substitution depended on the bulkiness of the ligands. Furthermore he reported [11] that no reduction of Co^{2+} occurred in presence of dppe. In contrast, we observed the conversion of Co^{2+} to $Co(CO)(dppe)_2^+$ under photolytic sensitization; $Co(CO)_3(PBu_3)_2^+$ was formed at a much faster rate in our sensitized reduction. In accord with Rigo's report [11], we observed precoordination of dppe even when $Co(acac)_2$ was used.

The structure of $Co(CO)(o\text{-}C_6H_4[PPh_2]_2)_2^+PF_6^-$ was determined by single crystal X-ray diffraction **. Table 2 lists selected bond distances and angles of the

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* A typical run is described for $Co(CO)(dppm)_2^+PF_6^-$. To a mixture of 0.053 g (0.30 mmol) of $Co(OAc)_2$ and 0.50 g (1.3 mmol) of dppm in a Pyrex tube was added THF (23 ml)/acetone (8 ml)/MeOH (5 ml). The solution was then irradiated while under an atmospheric pressure of CO. The photolysis was stopped after 4 h, and the solution has transferred into a flask containing an ethanol solution (20 ml) of $NH_4^+PF_6^-$. After 2 h the volume of the solution was reduced to about 2 ml, and 20 ml of H_2O was added. The complex $Co(CO)(dppm)_2^+PF_6^-$, a red precipitate, was removed by filtration, washed with water (20 ml × 5), ether (20 ml × 5), and dried.

** Red crystals were obtained by slow diffusion of Et_2O through a concentrated CH_3CN solution of $Co(CO)(o\text{-}C_6H_4[PPh_2]_2)_2^+PF_6^-$. It is orthorhombic, space group *Pbca*, a 19.701(5), b 24.850(13), c 21.865(9) Å, V 10704 Å^3, $Z = 8$, D_c 1.396 g cm^{-3}, $F(000) = 4623$, $\mu(\text{Mo-}K_\alpha)$ 5.3 cm^{-1}. Intensity data: Enraf–Nonius CAD-4 diffractometer, θ–2θ scan mode in the range $0 \leq 2\theta \leq 50°$; 4902 unique reflections ($I > 2.4\sigma(I)$). Absorption corrections according to ψ scans of three reflections were made. The structure was solved by direct methods (MULTAN) [12] and refined by full-matrix least squares. Final residuals were as follows: $R = 0.043$, $R_w = 0.055$.

Table 1

Elemental analyses and ν(CO) infrared, ^{31}P NMR data

Compound	Yield (%)	Analysis (%)		ν(CO) (cm^{-1}) [a]	^{31}P NMR (ppm) [b]
		C Found (calcd.)	H Found (calcd.)		
$Co(CO)_3(PBu_3)_2{}^+ BPh_4{}^-$	60	70.42 (70.59)	8.54 (8.54)	1991s	51.88(s)
$Co(CO)(dppm)_2{}^+ PF_6{}^-$	29	61.31 (61.21)	4.42 (4.43)	1959s	−0.06(s, 4P) [c]
$Co(CO)(dppe)_2{}^+ PF_6{}^-$	25	61.81 (61.81)	4.69 (4.67)	1938s	75.7(s, 4P) [c]
$Co(CO)(o\text{-}C_6H_4[PPh_2]_2)_2{}^+ PF_6{}^-$	62	64.76 (65.13)	4.54 (4.27)	1927s	67.77(s, 4P) [c]
$Fe(CO)_3(o\text{-}C_6H_4[PPh_2]_2)$	50	67.07 (67.50)	4.07 (4.09)	1988s, 1920sh 1906s	98.7(s)

[a] Measured in THF solution. [b] Measured in acetone-d_6 and are relative to δ(aqueous 85% H_3PO_4) 0 ppm. [c] $PF_6{}^-$ appeared as a septet at −138.43 ppm.

complex. The structure of $Co(CO)(o\text{-}C_6H_4[PPh_2]_2)_2{}^+$ (Fig. 1) is similar to most pentacoordinated Co^+ complexes that the geometry about the cobalt core is an approximate trigonal bipyramid, with the CO ligand occupying the equatorial position and the bite angles for the two $o\text{-}C_6H_4[PPh_2]_2$ ligands are 81.53(6) and 84.22(6)°. In contrast to $Co(CO)(dppm)_2{}^+$ [9], there is no apparent deviation of the two axial phosphorus ligands from the 180°, and the C(1)–Co–P_{eq}(2) and C(1)–Co–P_{eq}(4) are much larger than that of P_{eq}(1)–Co–P_{eq}(2). The ^{31}P NMR spectrum of $Co(CO)(o\text{-}C_6H_4[PPh_2]_2)_2{}^+$ clearly indicates that it is fluxional in solution, which is commonly observed in many complexes with trigonal-bipyramidal structure [13].

Table 2

Selected bond distances and angles for $Co(CO)(o\text{-}C_6H_4[PPh_2]_2)_2{}^+ PF_6{}^-$

Distances (Å)					
Co–P(1)	2.212(2)	Co–P(2)	2.266(2)	Co–P(3)	2.217(2)
Co–P(4)	2.242(2)	Co–C(1)	1.742(6)	P(1)–C(2)	1.824(5)
P(1)–C(8)	1.829(5)	P(1)–C(14)	1.831(5)	P(2)–C(7)	1.825(5)
P(2)–C(20)	1.836(5)	P(2)–C(26)	1.827(5)	P(3)–C(32)	1.833(6)
P(3)–C(38)	1.819(5)	P(3)–C(44)	1.838(5)	P(4)–C(33)	1.824(5)
P(4)–C(50)	1.840(5)	P(4)–C(56)	1.842(5)	P(5)–F(1)	1.494(5)
P(5)–F(2)	1.508(6)	P(5)–F(3)	1.502(6)	P(5)–F(4)	1.509(6)
P(5)–F(5)	1.460(6)	P(5)–F(6)	1.601(6)	C(1)–O(1)	1.148(7)

Angles (deg)			
P(1)–Co–P(2)	81.53(6)	P(1)–Co–P(3)	177.56(6)
P(1)–Co–P(4)	98.19(6)	P(1)–Co–C(1)	88.30(18)
P(2)–Co–P(3)	98.04(6)	P(2)–Co–P(4)	109.72(6)
P(2)–Co–C(1)	129.41(18)	P(3)–Co–P(4)	84.22(6)
P(3)–Co–C(1)	129.4(2)	P(4)–Co–C(1)	120.8(2)
Co–C(1)–O(1)	176.6(5)		

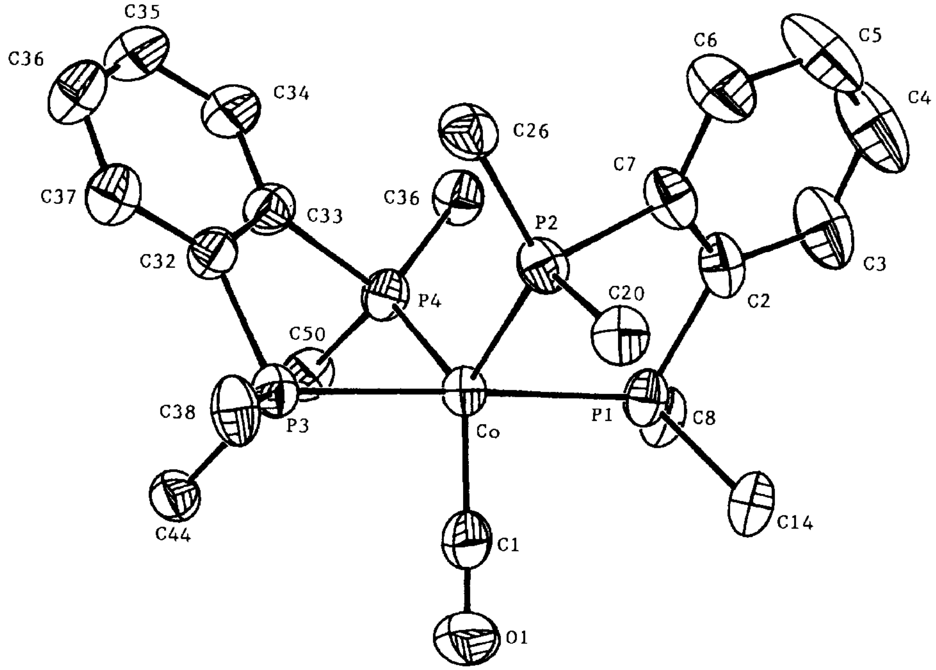

Fig. 1. ORTEP drawing of $Co(CO)(o\text{-}C_6H_4[PPh_2]_2)^+$. Eight phenyl groups are represented only by their *ipso* carbon atoms for clarity. The ellipsoids are drawn to 30% probability boundaries.

Sensitized photoreduction * of Fe^{II} also occurred readily under similar conditions to those for Co^{2+}. Complexes $Fe(CO)_4(PPh_3)$ and $Fe(CO)_3(L \sim L)$ ($L \sim L$ = $o\text{-}C_6H_4[PPh_2]_2$, $Ph_2CH_2PPh_2$, $PPh_2CH_2CH_2PPh_2$) were isolated **,***, depending on the phosphines used in the reaction. Studies are currently in progress as to the application of these sensitized photoreductions to the synthesis of organometallics.

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* Both $Fe(HCO_2)_2$ and $FeCl_2$ were tested for the reaction. However, triethylamine was needed in case of $FeCl_2$, to ensure a cleaner reaction. Triethylamine probably traps any hydrochloric acid that is formed during the reaction.

** The complexes $Fe(CO)_4$ [14], $Fe(CO)_3(Ph_2PCH_2PPh_2)$ [15], and $Fe(CO)_3(PPh_2CH_2CH_2PPh_2)$ [15] have the same spectroscopic properties as the authentic compounds. The formulation of $Fe(CO)_3(o\text{-}C_6H_4[PPh_2]_2)$ was further confirmed by a single crystal X-ray diffraction study: S.Y. Wang, J.T. Lin, unpublished results.

*** A typical run is described for $Fe(CO)_3(o\text{-}C_6H_4[PPh_2]_2)$: To a mixture of 0.089 g (0.70 mmol) of $FeCl_2$ and 0.39 g (0.87 mmol) of $o\text{-}C_6H_4[PPh_2]_2$ in a Pyrex tube was added THF (56 ml)/acetone (16 ml)/triethylamine (0.2 ml). The solution was then irradiated for 3 h under atmospheric pressure of CO. After removal of the solvent, the residue was treated with 20 ml of acetone and filtered. The filtrate was pumped dry and chromatographed on a silica column (230–400 mesh ASTM, Merck) using a 1/4 mixture of CH_2Cl_2/hexane as solvent. The yellow band was collected and the solvent removed to provide the yellow, powder of $Fe(CO)_3(o\text{-}C_6H_4[PPh_2]_2)$.

Supplementary material available. Tables of bond distances and angles (Tables S1, 4 pages), atomic coordinates (Table S2, 3 pages), anisotropic thermal parameters and hydrogen parameters (Table S3, 3 pages), and a listing of structure factors (62 pages), are available from the authors.

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