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Formation of $M(CO)_4^+$ (M = Co, Rh) by dissolution of neutral Co and Rh carbonyl clusters in strong acids under CO atmosphere

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Abstract

The dissolution of the neutral Co carbonyl cluster, $Co_2(CO)_8$, in HSO_3F or magic acid ($HSO_3F \cdot SbF_5$) under a CO atmosphere results in the formation of the Co(I) tetracarbonyl cation, $[Co(CO)_4]^+_{(solv)}$, and H_2. The IR and Raman spectra for $[Co(CO)_4]^+_{(solv)}$ suggest a trigonal bipyramidal structure in which two CO ligands together with a solvent ligand are in the equatorial plane, and the two axial CO ligands are in a nearly linear alignment. No cobalt carbonyl complexes are formed in less acidic solution such as 96% H_2SO_4. The dissolution of $Rh_4(CO)_{12}$ in concentrated H_2SO_4, HSO_3F or magic acid ($HSO_3F \cdot SbF_5$) under a CO atmosphere leads to the formation of the square-planar Rh(I) tetracarbonyl cation, $[Rh(CO)_4]^+$, and H_2, where Rh(0) is unusually oxidized to Rh(I) by H^+. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

Recently, there has been a rapid development in the preparation and structural characterization of homoleptic metal carbonyl cations and their relative cationic derivatives of metals from Groups 6–12, which are formed in superacids [1], strong acids such as concentrated H_2SO_4 [2], or with weakly coordinating anions [3]. Use of the metal carbonyl cations as catalysts for organic transformations has been reported [4,5]. For the Group 9 metals, Willner et al. reported that $[Ir(CO)_6]^{3+}$ is isolated by the reductive carbonylation of IrF_6 in SbF_5 [6a], and $[Rh(CO)_4]^+$ is formed by the solvolysis and carbonylation of $[RhCl(CO)_2]_2$ in HSO_3F [6b]. Very recently, the $[Rh(CO)_4]^+$ cation has been isolated from $[RhCl(CO)_2]_2$ using the superweak anion $1\text{-Et–}CB_{11}F_{11}^-$ [7]. In both of the cases, Rh retains the oxidation state of +1. The $[Rh(CO)_4]^+$ cation has been found to be an excellent catalyst for carbonylation of olefins to produce tertiary carboxylic acids in high yields in concentrated H_2SO_4 at room temperature and atmospheric pressure of CO [4a].

The protonation of neutral metal carbonyl clusters with a range of acids, particularly concentrated H_2SO_4, has been described; the dissolution of $Ir_4(CO)_{12}$, $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ in concentrated H_2SO_4 or anhydrous HF is known to give rise to the formation of protonated carbonyl clusters, $[Ir_4(CO)_{12}H_2]^{2+}$, $[Ru_3(CO)_{12}H]^+$ and $[Os_3(CO)_{12}H]^+$, respectively [8]. In this paper, we report that the dissolution of the neutral Co carbonyl cluster, $Co_2(CO)_8$, in superacidic media under a CO atmosphere results in the formation of a new cobalt(I) tetracarbonyl cation, $[Co(CO)_4]^+_{(solv)}$, and the dissolution of $Rh_4(CO)_{12}$ in concentrated H_2SO_4 or superacids in the presence of CO leads to the formation of $[Rh(CO)_4]^+$, which is a novel example for the oxidation of Rh(0) to Rh(I) by H^+.

2. Experimental

$Co_2(CO)_8$ and 96% H_2SO_4 were purchased from Kanto Chemical Co., Inc., $Rh_4(CO)_4$ and $Ir_4(CO)_4$ from Strem Chemicals, and HSO_3F and magic acid, $HSO_3F \cdot SbF_5$ (1:1), from Aldrich Chem. Co. The preparation of the Co(I) and Rh(I) carbonyl cations was carried out using a 100-ml three-necked flask con-

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nected to a CO gas buret, similar to the equipment used in the previous studies [4]. Standard canula transfer techniques were used for all sample manipulations for the spectroscopic measurements.

Infrared spectra were obtained at room temperature (r.t.) on thin films between two silicon discs on a JASCO FT/IR-230 spectrometer with a range of 4000–400 cm^{-1} and a spectral resolution of 2 cm^{-1}. Raman spectra were recorded at r.t. on a Nicolet FT-Raman 960 spectrometer with a range of 4000–100 cm^{-1} and a spectral resolution of 2 cm^{-1} using the 1064 nm exciting line (~ 600 mV) of a Nd:YAG laser (Spectra Physics, USA). Liquid Raman samples were contained in a 5-mm o.d. NMR tube. ^{1}H- and ^{13}C-NMR spectra were obtained at natural ^{13}C-abundance on a JEOL JNM-AL400 spectrometer. Liquid samples were contained in a 5 mm o.d. NMR tube, in which a coaxial insert of $CDCl_3$ as an external reference and a lock was placed. Chemical shifts are given in δ units (ppm) downfield from tetramethylsilane. H_2 was analyzed using a Hitachi M-2000 mass spectrometer and a Yanaco G3800 gas chromatograph with a column of 13X molecular sieves.

3. Results and discussion

In concentrated H_2SO_4 or anhydrous HF, $Ir_4(CO)_{12}$ is dissolved with the skeleton of the cluster unbroken to give a protonated species which was characterized as $[Ir_4(CO)_{12}H_2]^{2+}$ on the basis of an accurate integral of the hydride resonance against a weighed amount of the reference, Me_2SO_4 [8]. In the present work, we have investigated the interaction of $Ir_4(CO)_{12}$ with acids significantly stronger than those that have been previously used, and found that $[Ir_4(CO)_{12}H_2]^{2+}$ is also formed by dissolving $Ir_4(CO)_{12}$ in the superacids, HSO_3F, and magic acid, $HSO_3F \cdot SbF_5$ (1:1), as in concentrated H_2SO_4. Metal–metal bond stretching characteristically exhibits an intense band in the Raman spectrum [9]. The Raman spectra (Table 1), reported here for the first time, of the product from the reaction of $Ir_4(CO)_{12}$ in 96% H_2SO_4, HSO_3F and $HSO_3F \cdot SbF_5$ (1:1), show two sharp Raman bands at ca. 198 and 162 cm^{-1} for the Ir–Ir stretching vibrations with values similar to those observed for $Rh_4(CO)_{12}$ (221, 173 cm^{-1}) [9b], $[\{Pt(CO)_3\}_2]^{2+}$ (165 cm^{-1}) [2] and $[Hg_2(CO)_2][Sb_2F_{11}]_2$ (169 cm^{-1}) [10], confirming the presence of Ir–Ir bonds. The product exhibits one ^{1}H resonance for the

Table 1
IR, Raman and NMR data for $[Co(CO)_4]^{+}_{(solv)}$ and $[Rh(CO)_4]^{+}$ formed from neutral Co and Rh carbonyl clusters and the related protonated iridium carbonyl cluster, $[Ir_4(CO)_{12}H_2]^{2+}$, in various strong acids at room temperature [a]

Cation	Reagents	$\nu(CO)_{IR}$ (cm^{-1})	$\nu(CO)_{Raman}$ (cm^{-1})	$\delta(^{13}C)$ (ppm)
$[Co(CO)_4]^{+}_{(solv)}$ [b]	$Co_2(CO)_8$, CO, 96% H_2SO_4	–	–	–
	$Co_2(CO)_8$, CO, HSO_3F	2154w [c], 2139s [d], 2122s [e]	2194vs [f], 2155s [c], 2140w [d], 2129m [e]	182.1[g]
	$Co_2(CO)_8$, CO, $HSO_3F{\cdot}SbF_5$ (3:1)	2155w [c], 2139s [d], 2122s [e]	2194vs [f], 2155s [c], 2141w [d], 2128m [e]	183.9
	$Co_2(CO)_8$, CO, $HSO_3F{\cdot}SbF_5$ (1:1)	2155w [c], 2139s [d], 2122s [e]	2195vs [f], 2156s [c], 2141w [d], 2128m [e]	186.1
$[Rh(CO)_4]^{+}$	$Rh_4(CO)_{12}$, CO, 96% H_2SO_4	2139s	2215s, 2175s	171.5
	$Rh_4(CO)_{12}$, CO, HSO_3F	2141s	2216s, 2178s	171.5
	$Rh_4(CO)_{12}$, CO, $HSO_3F{\cdot}SbF_5$ (1:1)	2143s	2217s, 2179s	170.0
$[Ir_4(CO)_{12}H_2]^{2+}$	$Ir_4(CO)_{12}$, CO, 96% H_2SO_4	2175vw, 2155s, 2146s, 2123m, 2112m	2178s, 2121s[h]	144.2, 142.0 [h]
	$Ir_4(CO)_{12}$, CO, HSO_3F	2156s, 2149s, 2124m, 2115m	2179s, 2124s[i]	144.0, 141.9 [i]
	$Ir_4(CO)_{12}$, CO, $HSO_3F{\cdot}SbF_5$ (1:1)	2158s, 2151s, 2127m, 2116m	2180s, 2128s[j]	142.3, 140.2 [j]

[a] Abbreviations: s, strong; m, medium; w, weak; v, very; sym, symmetric; asym, asymmetric; eq, equatorial.

[b] Trigonal bipyramidal configuration with one coordination site in the equatorial plane occupied by a weakly coordinating solvent ligand; not formed in 96% H_2SO_4.

[c] Eq, sym.

[d] Axial, asym.

[e] Eq, asym.

[f] Axial, sym.

[g] At −5°C.

[h] ν(Ir–Ir) = 199, 163 cm^{-1}; $\delta(^{1}H) = -19.6$ ppm.

[i] ν(Ir–Ir) = 198, 163 cm^{-1}; $\delta(^{1}H) = -19.5$ ppm.

[j] ν(Ir–Ir) = 198, 162 cm^{-1}; $\delta(^{1}H) = -20.5$ ppm.

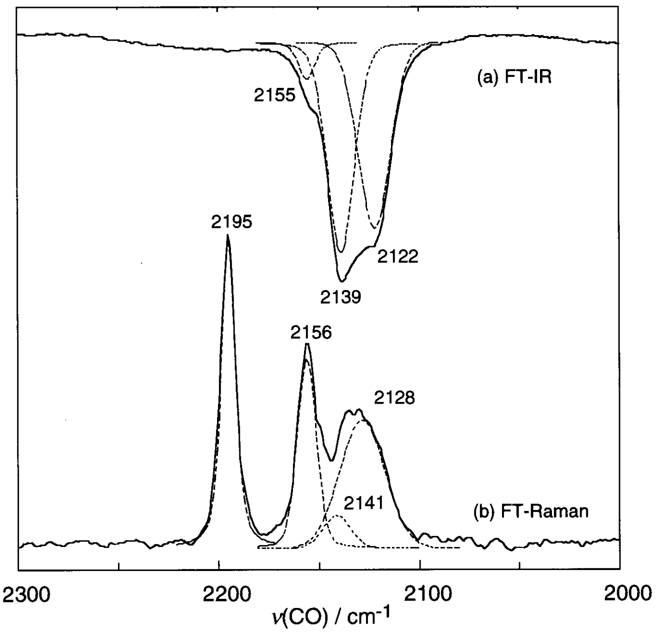

Fig. 1. FT-IR (a) and FT-Raman (b) spectra of $[Co(CO)_4]^+_{(solv)}$ formed by dissolution of $Co_2(CO)_8$ in magic acid, $HSO_3F{\cdot}SbF_5$(1:1), under a CO atmosphere at room temperature.

hydride, and two high-field ^{13}C resonances for the carbonyl groups, which are consistent with the previous reports [8]. $[Ir_4(CO)_{12}H_2]^{2+}$ is very stable in both of HSO_3F and $HSO_3F \cdot SbF_5$ even under evacuation or in the absence of gaseous CO.

In contrast, the dissolution of $Co_2(CO)_8$ and $Rh_4(CO)_{12}$ in the strong acids and superacids gives rise to the breaking of the metal–metal bonds in both the absence and presence of CO. In the absence of CO, the dissolution of $Co_2(CO)_8$ in 96% H_2SO_4, HSO_3F or magic acid readily leads to the loss of all the CO ligands and the oxidation of Co(0) to Co(II). Under a CO atmosphere, a new cobalt carbonyl species (yellow–brown) was readily formed by dissolving $Co_2(CO)_8$ in magic acid, which exhibits no Raman band due to ν(Co–Co) and no ^1H resonance due to a hydride. During the reaction, there was no CO uptake, but H_2 evolution was observed. By analyzing the gas phase using mass spectroscopy and gas chromatography, the amount of H_2 evolution was found to be exactly 1 mol per mol of $Co_2(CO)_8$, leading to the formulation of $[Co(CO)_4]^+_{(solv)}$ for the new cobalt carbonyl species (see Eq. (1)).

$$Co^0_2(CO)_8 + 2H^+ \rightarrow 2[Co^I(CO)_4]^+_{(solv)} + H_2 \qquad (1)$$

The IR and Raman spectra for $[Co(CO)_4]^+_{(solv)}$ (see Fig. 1 and Table 1) indicate a distortion away from planar geometry. As observed in many Co(I) complexes [11–13], a trigonal bipyramidal structure is suggested for the new $[Co(CO)_4]^+_{(solv)}$ complex formed in superacids, which includes two axial CO ligands and two equatorial CO ligands with another coordination site in the equatorial plane occupied by a weakly coordinating solvent ligand. The two axial CO ligands are in nearly linear alignment because the Raman band for the asymmetric stretch at 2141 cm^{-1} has a very small intensity, and the IR band for the symmetric stretch, corresponding to the Raman band at 2195 cm^{-1}, is too weak to be detected. The vibrational frequencies for $[Co(CO)_4]^+_{(solv)}$ in superacids are significantly higher than observed for related silylcobalt tetracarbonyls [11] and cobalt(I) carbonyl cations stabilized by donor ligands of phosphines, $Co(CO)_3P_2^+$ and $Co(CO)_4P^+$ [12]. Only one ^{13}C-NMR resonance at 186.1 ppm was observed for $[Co(CO)_4]^+_{(solv)}$ (Table 1), suggesting a rapid fluxional process between the axial and equatorial CO ligands.

It has been considered that a reversible disproportionation of $Co_2(CO)_8$ may be induced by CO under high pressure to form a very unstable ionic species $[Co(CO)_5^+][Co(CO)_4^-]$ [13]. Armentrout et al. have determined the sequential bond dissociation energies (D_0) of $Co(CO)_x^+$ ($x = 1$–5) at 0 K using guided-ion beam mass spectrometry [14a]; $D_0[(CO)_3Co^+{-}CO]$ (0.78 eV) is larger than $D_0[(CO)_3Cu^+{-}CO]$ (0.55 eV) [14b]. At room temperature, $[Co(CO)_4]^+_{(solv)}$ is stable under a CO atmosphere in magic acid for more than 2 days, but is extremely unstable in the absence of CO; by evacuation for several minutes, it loses CO ligands to give a light-pink Co^{2+} solution which exhibits no spectroscopic evidence for any cobalt carbonyl species. By lowering the acidity of the solution, $[Co(CO)_4]^+_{(solv)}$ decreases its stability. $[Co(CO)_4]^+_{(solv)}$ formed by the dissolution of $Co_2(CO)_8$ in HSO_3F under a CO atmosphere decomposes within several hours to give a light-pink colloidal Co^{2+} solution. $[Co(CO)_4]^+_{(solv)}$ can not be formed in 96% H_2SO_4; $Co_2(CO)_8$ is readily decomposed in 96% H_2SO_4 even under a CO atmosphere and oxidized to Co(II).

The dissolution of $Rh_4(CO)_{12}$ in concentrated H_2SO_4, HSO_3F or magic acid under a CO atmosphere at room temperature readily results in the formation of a yellow–brown solution, which is accompanied by H_2 evolution and CO uptake. No ^1H-NMR resonance was observed for a hydride and no Raman band due to ν(Rh–Rh) appeared, indicating that the product is mononuclear. Therefore, the neutral $Rh_4(CO)_{12}$ is oxidized by H^+ in the acids under a CO atmosphere to form the Rh(I) tetracarbonyl cation, $[Rh(CO)_4]^+$, according to Eq. (2); this is an unusual example of the oxidation of Rh(0) to Rh(I) by H^+.

$$Rh^0_4(CO)_{12} + 4CO + 4H^+ \rightarrow 4[Rh^I(CO)_4]^+ + 2H_2 \qquad (2)$$

There have only been related reports on the oxidation of anionic Rh and Ir carbonyl clusters, $[Rh_6C(CO)_{15}]^{2-}$ and $[Ir_6(CO)_{15}]^{2-}$, by H^+, the former giving rise to the formation of $[Rh_{12}C_2(CO)_{24}]^{2-}$ and H_2 [15,16], and the latter to the formation of $Ir_6(CO)_{16}$ and H_2 [15,17].

The vibrational and NMR data (see Table 1) for $[Rh(CO)_4]^+$ formed by the dissolution of $Rh_4(CO)_{12}$ in these acids are in keeping with those reported for the $[Rh(CO)_4]^+$ cation formed from $[RhCl(CO)_2]_2$ [6b, 7]. The observed vibrational bands for $[Rh(CO)_4]^+$, for example, the IR band at 2143 cm^{-1} (E_u) and the Raman bands at 2217 (A_{1g}) and 2179 (B_{1g}) cm^{-1} in $HSO_3F{\cdot}SbF_5$ (1:1), are entirely consistent with the square-planar structure (D_{4h}). Only a single ^{13}C resonance was observed for $Rh(CO)_4^+$ in concentrated H_2SO_4, HSO_3F or magic acid at room temperature. Although a coupling of $^{103}Rh-^{13}C$ is expected for $[Rh(CO)_4]^+$, the non-existence of a split for the ^{13}C resonance suggests a rapid CO exchange process between the Rh(I) carbonyl cations due to the significantly weak Rh–CO bond; it has been supported by the observations of line broadening for the ^{13}C resonance of $[Rh(CO)_4]^+$ in HSO_3F with lowering the temperature and the splitting to two peaks at temperatures below $-70°C$. By a brief evacuation, $[Rh(CO)_4]^+$ readily loses CO ligands to give a dark red–brown solution, which exhibits no IR and Raman bands in the CO stretching region and no ^{13}C-NMR resonance.

4. Conclusions

In the present work it was discovered that the dissolution of the neutral Co carbonyl cluster, $Co_2(CO)_8$, in HSO_3F or magic acid ($HSO_3F \cdot SbF_5$) under a CO atmosphere results in the formation of the Co(I) tetracarbonyl cation, $[Co(CO)_4]^+_{(solv)}$, and H_2. The IR and Raman measurements suggest a trigonal bipyramidal structure for $[Co(CO)_4]^+_{(solv)}$ in which two CO ligands together with a solvent ligand are in the equatorial plane, and the two axial CO ligands are nearly linear. The cobalt carbonyl cation is not formed in less acidic media. The dissolution of $Rh_4(CO)_{12}$ in concentrated H_2SO_4, HSO_3F or magic acid ($HSO_3F \cdot SbF_5$) under a CO atmosphere leads to the formation of the square-planar Rh(I) tetracarbonyl cation, $[Rh(CO)_4]^+$, and H_2, where Rh(0) is unusually oxidized to Rh(I) by H^+. The cluster fragmentation of $Co_2(CO)_8$ and $Rh_4(CO)_{12}$ in the strong acids and superacids is contrasted with the protonation of $Ir_4(CO)_{12}$ by the same acids to give the dication $[Ir_4(CO)_{12}H_2]^{2+}$.

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References

[1] (a) E. Bernhardt, B. Bley, R. Wartchow, H. Willner, E. Bill, P. Kuhn, I.H.T. Sham, M. Bodenbinder, R. Bröchler, F. Aubke, J. Am. Chem. Soc. 121 (1999) 7188. (b) H. Willner, F. Aubke, Angew. Chem. Int. Ed. Engl. 36 (1997) 2402.

[2] Q. Xu, Y. Souma, B.T. Heaton, C. Jacob, K. Kanamori, Angew. Chem. Int. Ed. Engl. 39 (2000) 208.

[3] (a) O.G. Polyakov, S.M. Ivanova, C.M. Gaudinski, S.M. Miller, O.P. Anderson, S.H. Strauss, Organometallics 18 (1999) 3769. (b) A.J. Luppinetti, S.H. Strauss, Chemtracts-Inorg. Chem. 11 (1998) 565.

[4] (a) Q. Xu, H. Nakatani, Y. Souma, J. Org. Chem. 65 (2000) 1540. (b) Q. Xu, Y. Souma, J. Umezawa, M. Tanaka, H. Nakatani, J. Org. Chem. 64 (1999) 6306. (c) Q. Xu, Y. Souma, Top. Catal. 6 (1998) 17. (d) Q. Xu, Y. Imamura, M. Fujiwara, Y. Souma, J. Org. Chem. 62 (1997) 1594.

[5] L. Weber, M. Barlmeyer, J.-M. Quasdorff, H.L. Sievers, H.-G. Stammler, B. Neumann, Organometallics 18 (1999) 2497.

[6] (a) C. Bach, H. Willner, C. Wang, S.J. Rettig, J. Trotter, F. Aubke, Angew. Chem. Int. Ed. Engl. 35 (1996) 1974. (b) C. Bach, Ph.D. Thesis, Hannover, 1999.

[7] A.J. Lupinetti, M.D. Havighurst, S.M. Miller, O.P. Anderson, S.H. Strauss, J. Am. Chem. Soc. 121 (1999) 11920.

[8] (a) S.A. Brewer, J.H. Holloway, E.G. Hope, J. Fluorine Chem. 70 (1995) 167. (b) J. Knight, M.J. Mays, J. Chem. Soc. A (1970) 711. (c) J. Knight, M.J. Mays, Chem. Commun. (1969) 384.

[9] (a) T. Spiro, Progr. Inorg. Chem. 11 (1970) 1. (b) W.P. Griffith, A.J. Wickham, J. Chem. Soc. A (1969) 834.

[10] (a) H. Willner, M. Bodenbinder, C. Wang, F. Aubke, J. Chem. Soc. Chem. Commun. (1994) 1189. (b) M. Bodenbinder, G. Balzer-Jöllenbeck, H. Willner, R.J. Batchelor, F.W.B. Einstein, C. Wang, F. Aubke, Inorg. Chem. 35 (1996) 82.

[11] (a) F.E. Saalfeld, M.V. McDowell, A.G. MacDiarmid, J. Am. Chem. Soc. 92 (1970) 2324. (b) A.P. Hagen, A.G. MacDiarmid, Inorg. Chem. 6 (1967) 686.

[12] (a) A.D. Zotto, P. Rigo, J. Organomet. Chem. 390 (1990) 97. (b) K.Y. Lee, J.K. Kochi, Inorg. Chem. 28 (1989) 567. (c) P. Rigo, M. Bressan, A. Morvillo, J. Organomet. Chem. 105 (1976) 263. (d) W. Hieber, H. Duchatsch, Chem. Ber. 98 (1965) 1744.

[13] S. Metlin, I. Wender, H.W. Sternberg, Nature 183 (1959) 457.

[14] (a) S. Goebel, C.L. Haynes, F.A. Khan, P.B. Armentrout, J. Am. Chem. Soc. 117 (1995) 6994. (b) F. Meyer, Y-M. Chen, P.B. Armentrout, J. Am. Chem. Soc. 117 (1995) 4071.

[15] (a) C.E. Barnes, Chapter 4, in: Comprehensive Organometallic Chemistry II, vol. 8, Pergamon, New York, 1995. (b) P. Chini, B.T. Heaton, Top. Curr. Chem. 71 (1977) 1.

[16] (a) V.G. Albano, D. Braga, P. Chini, D. Strumolo, S. Martinengo, J. Chem. Soc. Dalton Trans. (1983) 249. (b) B.T. Heaton, L. Strona, S. Martinengo, D. Strumolo, R.J. Goodfellow, I.H. Sadler, J. Chem. Soc. Dalton Trans. (1982) 1499. (c) P. Chini, J. Organomet. Chem. 200 (1980) 37.

[17] L. Malatesta, G. Caglio, M. Angoletta, Chem. Commun. (1970) 532.