Carbidoheptarhenate Cluster Complexes of Cadmium and Zinc Units: The Structure of $[PPh_4]_2[Re_7C(CO)_{21}(\mu_3\text{-}ZnCl)]$

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Introduction

As part of our investigation of carbidoheptarhenate cluster complexes of mercury units, with the general formula $[Re_7C(CO)_{21}(\mu_3\text{-HgX})]^{2-}$,[1−4] we became interested in extending this chemistry to include the lighter group 12 congeners, namely, cadmium and zinc. A recent discussion of cluster complexes with various bonds between transition elements and zinc, cadmium, or mercury is available.[5] However, we have found only one example of a cadmium or zinc unit bound to the face of a metal cluster framework, specifically, the zinc iodide−platinum complex $Pt_3(CO)_3(PPh(i\text{-}Pr)_2)_3(\mu_3\text{-}ZnI_2)$.[6] We now wish to report the synthesis and characterization of some carbidoheptarhenate cluster complexes of cadmium and zinc units together with the crystal structure of the zinc chloride complex, $[PPh_4]_2[Re_7C(CO)_{21}(\mu_3\text{-}ZnCl)]$. This is the first structurally characterized compound involving a rhenium−zinc bond.

Experimental Section

General Procedures. All reactions were carried out at room temperature by using standard inert atmosphere techniques. Solvents were distilled from appropriate drying agents under nitrogen before use. The compound $[PPh_4]_3[Re_7C(CO)_{21}]$ was prepared as previously described.[7,8] The reagents cadmium chloride (Aldrich), cadmium nitrate tetrahydrate (Aldrich), and 4-bromothiophenol (Aldrich) were used as received. Zinc chloride (Fisher) was recrystallized from methanol prior to use. IR spectra were recorded on Perkin-Elmer 1600 or 1750 FT-IR spectrometers. Negative-ion electrospray ionization mass spectra (ESI) were obtained on a VG Quattro spectrometer by the staff of the Mass Spectrometry Laboratory in the School of Chemical Sciences (SCS) at the University of Illinois. Elemental analyses were performed by the staff of the SCS Microanalytical Laboratory.

Synthesis of $[PPh_4]_2[Re_7C(CO)_{21}CdCl]$ (1). A sample of $[PPh_4]_3[Re_7C(CO)_{21}]$ (57.9 mg, 0.0198 mmol) and excess $CdCl_2$ (25.5 mg, 0.139 mmol) were combined in a 50 mL Schlenk tube, and 20 mL of acetone was added. The resulting solution was stirred for 15 min, until the color changed from deep red to brown, and the reaction was judged complete (IR). The solution was then evaporated to dryness under vacuum. The residue was dissolved in minimal dichloromethane (1 mL), and the solution was filtered through Celite. The filtrate was layered with 2-propanol (10 mL), and after 4 d, the lightly colored supernatant was decanted. The brown crystalline solid that remained was washed sequentially with methanol and diethyl ether, and then it was dried under vacuum (37.9 mg, 0.0139 mmol, 70%). Anal. Calcd for $C_{70}H_{40}CdClO_{21}P_2Re_7$: C, 30.79; H, 1.48. Found: C, 30.79; H, 1.51. IR (CH_2Cl_2): ν(CO), 2055 (w), 2001 (vs), 1971 (w), 1949 (w), 1923 (w), 1887 (vw) cm^{-1}. ESI−MS (^{187}Re, ^{114}Cd): *m/e* 2397 $\{[PPh_4][Re_7C(CO)_{21}CdCl]\}^-$, 1029 $\{[Re_7C(CO)_{21}CdCl]\}^{2-}$.

Synthesis of $[PPh_4]_2[Re_7C(CO)_{21}ZnCl]$ (2). The reaction was conducted as for **1** with 112.9 mg (0.0386 mmol) of $[PPh_4]_3[Re_7C(CO)_{21}]$ and 30.5 mg (0.224 mmol) of $ZnCl_2$ in 15 mL of acetone. From dichloromethane/hexanes, dark crystals of **2** (95.1 mg, 0.0354 mmol, 76%) were isolated. Anal. Calcd for $C_{70}H_{40}ClO_{21}P_2Re_7Zn$: C, 31.33; H, 1.50. Found: C, 31.36; H, 1.53. IR (CH_2Cl_2): ν(CO), 2057 (w), 2002 (vs), 1975 (w), 1950 (w), 1928 (w), 1891 (vw) cm^{-1}. ESI−MS (^{187}Re, ^{64}Zn): *m/e* 2347 $\{[PPh_4][Re_7C(CO)_{21}ZnCl]\}^-$, 2248 $\{[PPh_4][Re_7C(CO)_{21}]\}^-$. Single crystals of $[PPh_4]_2[Re_7C(CO)_{21}ZnCl]$ suitable for X-ray diffraction were selected directly from the bulk sample.

Synthesis of $[PPh_4]_2[Re_7C(CO)_{21}CdNO_3]$ (3). In a 20 mL Schlenk tube was dissolved a sample of $[PPh_4]_3[Re_7C(CO)_{21}]$ (30.6 mg, 0.0105 mmol) in 8 mL of dichloromethane. Then, a solution of 11 mg (0.036 mmol) of $Cd(NO_3)_2\cdot 4H_2O$ in 2 mL of acetone was added. The resulting solution was stirred for 15 min and then evaporated to dryness under vacuum. The residue was redissolved in minimal dichloromethane (1 mL), and the solution was filtered through Celite. The filtrate was layered with 2-propanol (10 mL), and after 4 days, the nearly colorless supernatant was decanted. The brown crystalline solid that was obtained was washed with methanol and diethyl ether and then dried under vacuum (20.3 mg, 0.00736 mmol, 70%). Anal. Calcd for $C_{70}H_{40}CdNO_{24}P_2Re_7$: C, 30.50; H, 1.46; N, 0.51. Found: C, 30.54; H, 1.54; N, 0.23. IR (CH_2Cl_2): ν(CO), 2055 (vw), 2001 (vs), 1971 (w), 1949 (w), 1923 (w), 1885 (vw) cm^{-1}. ESI−MS (^{187}Re, ^{114}Cd): *m/e* 2424 $\{[PPh_4][Re_7C(CO)_{21}CdNO_3]\}^-$, 1043 $\{[Re_7C(CO)_{21}CdNO_3]\}^{2-}$.

An analogous reaction was conducted to form the compound $[PPh_4]_2[Re_7C(CO)_{21}ZnNO_3]$ (**4**), which was characterized by its IR spectrum in CH_2Cl_2: ν(CO), 2056 (vw), 2002 (vs), 1973 (w), 1949 (w), 1925 (w), 1885 (vw) cm^{-1}.

Synthesis of $[PPh_4]_2[Re_7C(CO)_{21}CdSC_6H_4Br]$ (5). Samples of $[PPh_4]_2[Re_7C(CO)_{21}CdNO_3]$ (20.7 mg, 0.00751 mmol) and 4-bromothiophenol (1.7 mg, 0.0090 mmol) were dissolved in 10 mL of dichloromethane in a 20 mL Schlenk tube. The solution was stirred for 12 h and then evaporated to dryness under vacuum. The residue was redissolved in minimal dichloromethane (1 mL), and the solution was filtered. The filtrate was layered with methanol (10 mL), and after standing for 6 days, the supernatant was decanted. The dark crystalline solid that remained was washed with methanol and diethyl ether and then dried under vacuum (4.0 mg, 0.0014 mmol, 18%). Anal. Calcd for $C_{76}H_{44}BrCdO_{21}P_2Re_7S$: C, 31.66; H, 1.54. Found. C, 31.24; H, 1.67. IR (CH_2Cl_2): ν(CO), 2054 (w), 1999 (vs), 1970 (w), 1947 (w), 1922 (w), 1887 (vw) cm^{-1}. ESI−MS(^{187}Re, ^{114}Cd): *m/e* 2549 $\{[PPh_4][Re_7C(CO)_{21}CdSC_6H_4Br]\}^-$, 1105 $\{[Re_7C(CO)_{21}CdSC_6H_4Br]\}^{2-}$.

X-ray Crystal Structure Determination. A summary of selected crystallographic data for compound **2** is given in Table 1. The data set was collected on a Siemens Platform/CCD automated diffractometer. The structure was solved by direct methods;[9] hydrogen atoms were fixed on calculated positions. The structure was refined by full-matrix least-squares procedures,[10] based on F^2, of the positional, isotropic, and anisotropic thermal parameters. A structural diagram of **2** with its crystallographic labeling scheme and 35% thermal probability ellipsoids is shown in Figure 1. Table 2 provides selected bond lengths and angles for **2**.

Results and Discussion

Synthesis and Solution Behavior of Complexes. Combining the cluster compound $[PPh_4]_3[Re_7C(CO)_{21}]$ with excess MCl_2

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[1] Brand, U.; Shapley, J. R. *Inorg. Chem.* **2000**, *39*, 32.

[2] Brand, U.; Shapley, J. R. *Inorg. Chem.* **1998**, *37*, 5697.

[3] Brand, U.; Coffer, J. L.; Henly, T. J.; Wilson, S. R.; Shapley, J. R. *Inorg. Chem.* **1997**, *36*, 3386.

[4] Henly, T. J.; Shapley, J. R. *Organometallics* **1989**, *8*, 2729.

[5] Rosenberg, E.; Hardcastle, K. I. In *Comprehensive Organometallic Chemistry II*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Elsevier: Oxford, U.K., 1995; Vol 10, Chapter 6, p 323.

[6] Stockhammer, A.; Dahmen, K.-H.; Gerfin, T.; Venanzi, L. M.; Gramlich, V.; Petter, W. *Helv. Chim. Acta* **1991**, *74*, 989.

[7] Hayward, C.-M. T.; Shapley, J. R. *Organometallics* **1988**, *7*, 448.

[8] Brand, U.; Shapley, J. R. *Inorg. Chem.* **1997**, *36*, 253.

[9] Sheldrick, G. M. *SHELXTL*; Siemens Analytical X-ray Instruments, Inc.: Madison, WI, 1990.

[10] Sheldrick, G. M. *SHELXTL PC, Version 5.0*; Siemens Industrial Automation, Inc.: Madison, WI, 1994.

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Table 1. Crystallographic Data for $[PPh_4]_2[Re_7C(CO)_{21}ZnCl]$ (**2**)

formula	$C_{70}H_{40}ClO_{21}P_2Re_7Zn$
fw	2652.21
space group	$P\bar{1}$
T (K)	173(2)
a (Å)	13.4464(15)
b (Å)	13.6527(16)
c (Å)	22.843(3)
α(deg)	102.663(2)
β(deg)	91.869(2)
γ(deg)	119.104(2)
V (Å^3)	3526.9(7)
Z	2
D_{calcd} (g/cm^3)	2.497
μ(Mo Kα) (cm^{-1})	124.28
λ(Mo Kα) (Å)	0.71073
R1[a]	0.0567
wR2 (all data)[b]	0.1465

[a] $R1 = \sum|(F_o - F_c)|/\sum F_o$. [b] $wR2 = \{\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4\}^{1/2}$.

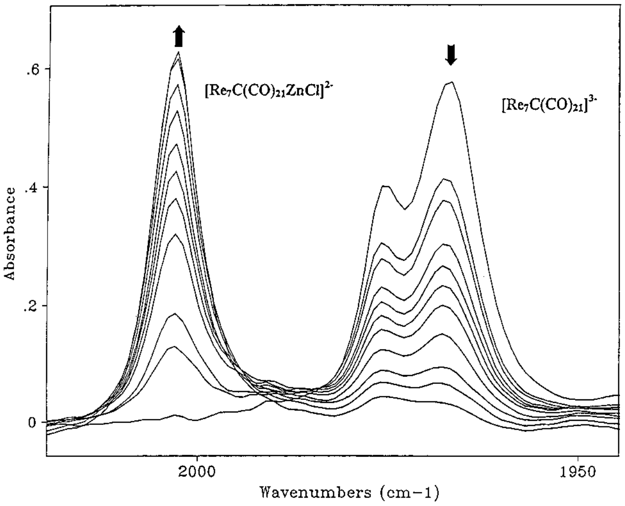

Figure 1. IR spectra of $[PPN]_3[Re_7C(CO)_{21}]$ (1.26×10^{-4} M) in acetone with different concentrations of added $ZnCl_2$ ($0-7.6 \times 10^{-2}$ M).

(M = Cd, Zn) in acetone provides the complexes $[PPh_4]_2[Re_7C(CO)_{21}(MCl)]$ (M = Cd, **1**; M = Zn, **2**) in good yields after evaporation of the reaction solvent and recrystallization of the residue from dichloromethane/2-propanol for **1** or dichloromethane/hexanes for **2**. Synthesis of the corresponding nitrate derivatives (**3**, **4**) is best accomplished in a less polar solvent mixture of acetone and dichloromethane. The IR spectra of these complexes dissolved in dichloromethane show only the intense band near 2000 cm^{-1} expected for such adducts.[11] However, the spectra of isolated compounds dissolved again in acetone show prominent peaks due to $[Re_7C(CO)_{21}]^{3-}$, indicating dissociation of the capping unit in the coordinating solvent. Qualitatively, the nitrate complexes **3** and **4** appear to dissociate to a relatively greater extent. Similar dissociative behavior was reported for the thallium(I) carbidoheptarhenate cluster complex $[Re_7C(CO)_{21}Tl]^{2-}$,[8] and it was invoked previously to explain the low stability of group 11 units attached to $[Re_6C(CO)_{19}]^{2-}$.[12]

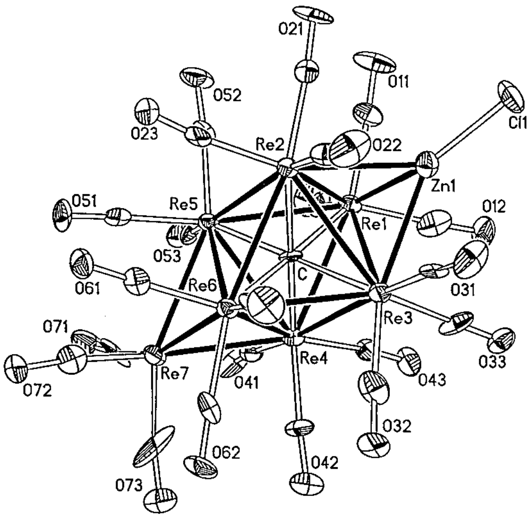

Figure 2. ORTEP diagram of the cluster anion in $[PPh_4]_2[Re_7C(CO)_{21}ZnCl]$ (**2**).

IR spectra for $[Re_7C(CO)_{21}]^{3-}$ in acetone with different concentrations of added $CdCl_2$ or $ZnCl_2$ were collected in order to assess the complexation equilibrium (eq 1). The set of

$$[PPh_4]_3[Re_7C(CO)_{21}] + MCl_2 \leftrightarrow [PPh_4]_2[Re_7C(CO)_{21}(MCl)] + PPh_4Cl \quad (1)$$

spectra obtained for zinc chloride is shown in Figure 1. Nonlinear least-squares fits of the equilibrium expression to absorbance data at both peak maxima[13] provided values of $8(1) \times 10^{-3}$ for M = Zn and 3.0(5) for M = Cd. Since the corresponding reaction appears to be quantitative for the carbidoheptarhenate mercury complex ($K \geq 10^4$),[4] the relative ranking of Zn < Cd ≪ Hg for the association constants toward the carbidoheptarhenate cluster face is quite consistent with the behavior of these metal ions toward other "soft" centers such as iodide.[14]

X-ray Crystallographic Study of 2. The molecular structure of the cluster anion in **2** is depicted in Figure 2. It contains an octahedron of rhenium atoms, centered on an interstitial carbon atom, with rhenium tricarbonyl and zinc chloride units capping trans (1,4) faces. This is the characteristic geometry found previously for carbidoheptarhenate complexes,[15,16] in particular, the mercury-capped dervivatives.[1-3] The average Re−Re distances for the zinc-capped face in **2** are ca. 0.05 Å longer than those for the uncapped faces, which average 2.98 Å. This is a smaller expansion than that in the case of the mercury-capped clusters, where the Re−Re distances of the capped face are ca. 0.08 Å longer; this difference is likely due to the smaller size of zinc as a capping atom. The Re−Zn bond distances, 2.689(2), 2.700(2), and 2.744(2) Å, indicate a relatively symmetrical, μ_3-face capping interaction. No examples of a Re−Zn bond distance were found in the literature for comparison, but the average distance of 2.71 Å may be compared with average distances of ca. 2.88 Å in the corresponding mercury derivatives.[1-3] The implied difference in covalent radius is similar to that suggested by comparing M−N distances in four-coordinate

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(11) This characteristic IR band of carbidoheptarhenate complexes is extremely intense. The molar absorption coefficient directly determined for the HgCl complex is 7.0×10^4 cm^{-1} M^{-1}, and the analogous best fit parameter for the ZnCl complex **2** is 5.3×10^4 cm^{-1} M^{-1}.

(12) Beringhelli, T.; D'Alfonso, G. D.; Molinari, H.; Sironi, A. *J. Chem. Soc., Dalton Trans.* **1992**, 689.

(13) Billo, E. J. *Excel for Chemists: A Comprehensive Guide*; Wiley-VCH: New York, 1997; Chapter 20, p 323.

(14) Cotton, F. A.; Wilkinson, G.; Murillo, C. A.; Bochmann, M. *Advanced Inorganic Chemistry*, 6th ed.; Wiley: New York, 1999; p 608.

(15) Beringhelli, T.; D'Alfonso, G.; Freni, M.; Ciani, G.; Sironi, A. *J. Organomet. Chem.* **1985**, *295*, C7.

(16) Henly, T. J.; Shapley, J. R.; Rheingold, A. L. *J. Organomet. Chem.* **1986**, *310*, 55.

Table 2. Selected Structural Parameters for $[PPh_4]_2[Re_7C(CO)_{21}ZnCl]$

bond distances (Å)

Zn1−Cl1	2.119(6)	Zn1−Re1	2.700(2)	Zn1−Re2	2.744(2)
Zn1−Re3	2.689(2)	Re1−Re2	3.0247(10)	Re1−Re3	3.0302(9)
Re2−Re3	3.0300(9)	Re1−Re4	3.0133(10)	Re1−Re5	2.9993(10)
Re2−Re5	3.0204(11)	Re2−Re6	2.9769(10)	Re3−Re4	2.9815(11)
Re3−Re6	2.9948(10)	Re4−Re5	2.9685(8)	Re4−Re6	2.9832(9)
Re5−Re6	2.9933(9)	Re4−Re7	2.9203(11)	Re5−Re7	2.9720(11)
Re6−Re7	2.9626(11)	Re1−C	2.123(13)	Re2−C	2.165(14)
Re3−C	2.148(15)	Re4−C	2.071(14)	Re5−C	2.102(15)
Re6−C	2.126(13)				

bond angles (deg)

Re1−Zn1−Re2	67.50(5)	Re1−Zn1−Re3	68.42(6)
Re2−Zn1−Re3	67.79(5)	Re1−Re2−Zn1	55.57(5)
Re2−Re1−Zn1	56.93(4)	Re1−Re3−Zn1	55.96(5)
Re2−Re3−Zn1	56.96(4)	Re3−Re2−Zn1	55.25(5)
Re3−Re1−Zn1	55.61(5)	Re1−Zn1−Cl1	140.5(2)
Re2−Zn1−Cl1	135.6(2)	Re3−Zn1−Cl1	143.0(2)
Zn1−Re1−C	85.9(5)	Zn1−Re2−C	84.1(4)
Zn1−Re3−C	85.7(4)	Zn1−Re1−C11	72.7(6)
Zn1−Re1−C12	80.4(6)	Zn1−Re1−C13	157.9(6)
Zn1−Re2−C21	75.7(5)	Zn1−Re2−C22	77.1(5)
Zn1−Re2−C23	157.9(5)	Zn1−Re3−C31	71.8(5)
Zn1−Re3−C32	157.3(6)	Zn1−Re3−C33	89.6(6)

pyrazolylborate complexes of mercury (ca. 2.27 Å)[17] and zinc (ca. 2.06 Å).[18] The Zn−Cl bond distance in complex **2** is 2.119(6) Å. This distance is slightly shorter than distances recently reported for four-coordinate L_3Zn-Cl complexes, which range from 2.148 to 2.308 Å.[18−29] However, a wide range of Zn−Cl distances can be found in four-coordinate zinc complexes, as illustrated in the structure of $[NH_4]_2[ZnCl_4]$, where the range is from 2.11(2) to 2.40(2) Å.[30] The trigonal pyramidal coordination geometry for the zinc atom in **2** has average Re−Zn−Cl bond angles of 139.7° and Re−Zn−Re bond angles of 67.9° compared with that in more typical four-coordinate L_3Zn-Cl complexes with values close to 125 and 95°, respectively.[18−29]

Reactivity of the Capping Unit. When the cadmium nitrate complex **3** was treated with 4-bromothiolphenol in dichloromethane, a slow reaction occurred to form the cadmium thiolate complex **5** in a low isolated yield. Efforts to complete an analogous reaction with the zinc-capped cluster were unsuccessful due to decomposition. In contrast, treatment of the analogous mercury hydroxide or mercury acetate complexes with thiols proceeds with substitution in a high yield.[2,3] Unfortunately, the ease with which the lighter group 12 metal caps dissociate from the carbidoheptarhenate complex under polar conditions severely limits prospects for any systematic study of the coordination chemistry at these pseudotetrahedral zinc or cadmium centers.

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Supporting Information Available: X-ray crystallographic file in CIF format for $[PPh_4]_2[Re_7C(CO)_{21}ZnCl]$ (**2**). This material is available free of charge via the Internet at http://pubs.acs.org.

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(17) Lobbia, G. G.; Cecchi, P.; Gobetto, R.; Digilio, G.; Spagna, R.; Camalli, M. *J. Organomet. Chem.* **1997**, *539*, 9.

(18) Yoon, K.; Parkin, G. *J. Am. Chem. Soc.* **1991**, *113*, 8414.

(19) Looney, A.; Cornebise, M.; Miller, D.; Parkin, G. *Inorg. Chem.* **1992**, *31*, 989.

(20) Tuntulani, T.; Reibenspies, J. H.; Farmer, P. J.; Darensbourg, M. Y. *Inorg. Chem.* **1992**, *31*, 3497.

(21) Hartmann, F.; Kläui, W.; Kremer-Aach, A.; Mootz, D.; Strerath, A.; Wunderlich, H. *Z. Anorg. Allg. Chem.* **1993**, *619*, 2071.

(22) Krieger, M.; Gould, R. O.; Neumüller, B.; Harms, K.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **1994**, *624*, 1434.

(23) LeCloux, D. D.; Keyes, M. C.; Osawa, M.; Reynolds, V.; Tolman, W. B. *Inorg. Chem.* **1994**, *33*, 6361.

(24) Phillips, J. R.; Poat, J. C.; Slawin, A. M. Z.; Williams, D. J.; Wood, P. T.; Woollins, J. D. *J. Chem. Soc., Dalton Trans.* **1995**, 2369.

(25) Nakata, K.; Uddin, M. K.; Ogawa, K.; Ichikawa, K. *Chem. Lett.* **1997**, 991.

(26) Cronin, L.; Greener, B.; Foxon, S. P.; Heath, S. L.; Walton, P. H. *Inorg. Chem.* **1997**, *36*, 2594.

(27) Eichhöfer, A.; Fenske, D.; Pfistner, H.; Wunder, M. *Z. Anorg. Allg. Chem.* **1998**, *624*, 1909.

(28) Dean, P. A. W.; Payne, N. C.; Wranich, J.; Vittal, J. J. *Polyhedron* **1998**, *17*, 2411.

(29) Fuhr, O.; Fenske, D. *Z. Anorg. Allg. Chem.* **1999**, *625*, 1229.

(30) Mikhail, I. *Acta Crystallogr.* **1980**, *B36*, 2126.