Table I. Bond lengths (Å) and angles (deg) for $[(C_6H_{11})_2NH_2]_2[Zn_2(SC_6H_5)_6]$ (**1**), $[(C_6H_5)_4P]_2[Zn_2(SC_6H_5)_6]$ (**2**), and $[(C_2H_5)_4N]_2[Zn_2(SC_2H_5)_6]$ (**3**)

atoms	1[a]	2[b-d]	3[c-e]
Zn···Zn	3.220 (1)	3.421 (1)	3.179 (1)
Zn(1)-S_t(1)	2.298 (2)	2.293 (1)	2.296 (1)
Zn(1)-S_t(2)	2.299 (2)	2.302 (1)	2.304 (1)
Zn(2)-S_t(5)	2.280 (2)		
Zn(2)-S_t(6)	2.292 (2)		
Zn(1)-S_b(4)	2.411 (2)	2.424 (1)	2.394 (1)
Zn(2)-S_b(3)	2.452 (2)	2.431 (1)	2.456 (1)
Zn(1)-S_b(3)	2.399 (2)		
Zn(2)-S_b(4)	2.386 (2)		
S_b(3)-Zn(1)-S_b(4)	96.22 (5)	90.7 (1)	98.1 (1)
S_b(3)-Zn(2)-S_b(4)	95.48 (5)		
S_t(1)-Zn(1)-S_t(2)	124.51 (6)		
S_t(5)-Zn(2)-S_t(6)	128.66 (6)	111.2 (1)	113.9 (1)
Zn(1)-S_b(3)-Zn(2)	83.16 (5)		
Zn(1)-S_b(4)-Zn(2)	84.33 (5)	89.3 (1)	81.9 (1)

[a] This work. [b] Reference 5. [c] This molecule has a center of inversion. [d] Atom numbering for this complex has been reassigned in this table. [e] Reference 8.

angle, 83.75 (5)°. An ideal edge-shared tetrahedral dimer possesses bridging angles of 70.5°.[10] Departures from this value are common for the hexakis(thiolato)dizincates[5,8] and hexachlorodizincates,[11-17] which feature Zn-L-Zn angles in the vicinity of 87°. In **2**, the Zn-S_b-Zn angle is 89.3 (1)° (Table I).[5] The larger angle in **2** correlates with a longer Zn-Zn distance, 3.421 (1) Å, as compared with that of **1**, 3.220 (1) Å (Table I). Hydrogen bonding to the terminal sulfur atoms is accompanied by a corresponding reduction in the Zn-S_b distance. This may be due to the removal of electron density on the metal through the hydrogen-bonded terminal sulfur ligands.[18] The ethanethiolate Zn dimer[8] is unusual with its small Zn-S_b-Zn angle and Zn···Zn separation relative to those of **1** and **2**. The large bridging angle in **1** gives rise to an average S_b-Zn-S_b angle of 95.85 (5)°, well below the ideal tetrahedral value. The reduced average Zn-S_b bond distance is indicative of a stabilizing influence of hydrogen bonding.[4]

A combination of reduced steric interactions and the availability of two lone electron pairs probably favors hydrogen bonding to the terminal sulfur ligands. Similar results are reported for the crystal structure of rat liver MT, where N-H···S hydrogen bonds with distances less than 3.5 Å occur only to cysteine residues which occupy terminal positions in the metal-cysteine binding arrangement of the protein.[3]

Far-IR Metal-Ligand Frequencies. Assuming local D_{2h} symmetry for the Zn_2S_6 framework of **1**, eight IR-active metal-ligand modes are expected, five of which correspond to terminal metal-ligand vibrations, which would be sensitive to hydrogen bonding. In keeping with assignments suggested for monomeric anionic complexes $[M(SC_6H_5)_4]^{2-}$, bands above 280 cm^{-1} are assigned to counterion and ligand internal vibrational modes.[4] Bands observed at 246, 232, 196, and 178 cm^{-1} in the IR spectrum of **1** can therefore reasonably be ascribed to metal-ligand modes. The two highest bands are assigned to terminal metal-ligand modes and the two lowest to bridging metal-ligand modes. These assignments are based on a comparison with the spectrum of the complex Fe_2Cl_6,[19] which has D_{2h} symmetry.[20] For this simple structure, the four highest far-IR peaks, at 468, 406, 328, and 280 cm^{-1}, are assigned to the ν_8 (t), ν_{16} (t), ν_{13} (b), and ν_{17} (b) stretching vibrations, respectively[19] (t = terminal modes; b = bridging modes). In **1** the bands corresponding to ν_8 and ν_{16} are expected to shift upon deuteration. However, the spectrum of $[(C_6H_{11})_2ND_2]_2[Zn_2(SC_6H_5)_6]$, recorded at 4-$cm^{-1}$ resolution, reveals frequency shifts no greater than ±1 cm^{-1}, with bands now observed at 246, 233, 195, and 179 cm^{-1}. Only one of the three frequency shifts occurs in a band assignable to a terminal metal-ligand mode which should be affected by H/D exchange to an extent greater than the bridging metal-ligand modes. We therefore do not consider the frequency shifts to arise from *local* effects of H/D exchange on metal-ligand bond strengths or normal modes. They likely result from overall changes in anion-cation distances and effects on crystal packing.

Conclusion. The shortened bond lengths of the Zn-S_b bonds suggest that the bridging framework of **1** is stabilized by hydrogen bonding. Similar N-H···S hydrogen bonding occurs in MT, albeit with amide N-H as the predominant hydrogen-bond donor.[3] The results obtained herein suggest that the hydrogen bonds in the protein may exert a similar stabilizing influence on the metal centers of the protein.

Supplementary Material Available: General structure report for compound **1** including a textual presentation of the details of the structure determination, listings of experimental details, positional and thermal parameters, inter- and intramolecular bond distances and bond angles involving non-hydrogen atoms, and intermolecular distances involving hydrogen atoms, and an ORTEP diagram of the structure, a table of selected far-IR bands for **1** and its deuterated ammonium derivative, and a figure showing the vibrational spectrum of **1** (60 pages); a listing of final observed and calculated structure factors (31 pages). Ordering information is given on any current masthead page.

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Stereoselectivity in the Oxidation of Horse Cytochrome *c* by $[Co(ox)_3]^{3-}$

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Over the past decade, significant advances have been made in the detection and interpretation of chiral induction in outer-sphere electron-transfer reactions involving metal ion complexes.[3-5] Electron-transfer metalloproteins are chiral reagents that might be expected to show considerable enantioselectivity, but few investigations of chiral induction in their reactions with metal ion complexes have been reported. Early studies failed to detect rate differences for Δ- and Λ-$[Co(en)_3]^{3+}$ with parsley ferredoxin[6] and for Δ- and Λ-$[Co(sep)]^{2+}$ with horse cytochrome *c*.[7] However,

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it cannot be concluded that stereoselectivity is absent in these reactions, merely that the effects are not sufficiently large to allow kinetic detection. Circular dichroism studies of product solutions provide a more sensitive detection method.[3,4] More recently, Bernauer and co-workers have reported rate ratios, k_Δ/k_Λ, as high as 1.63 for reactions of enantiomeric iron(II) complexes with spinach plastocyanin[8] and similar numbers for the corresponding cobalt(III) complexes with spinach ferredoxin.[9] Sakaki and co-workers have employed product analysis studies to determine stereoselectivity in the oxidation of horse cytochrome *c* by [Co(acac)$_3$].[10] In this latter study, the stereoselectivity is very small and shows a strong dependence on solvent, pH, and buffer.

In this paper, stereoselectivity is investigated in the oxidation of horse cytochrome *c* by $[Co(ox)_3]^{3-}$. This particular reaction is relatively well characterized, and two previous kinetic studies have been reported.[11,12] The negative charge on the oxidant is thought to promote interactions with positively charged lysine residues on the surface of the protein near the exposed heme edge active site, and indeed, NMR studies with the paramagnetic analogue $[Cr(ox)_3]^{3-}$ have been used to pinpoint amino acid residues important in the binding site.[13,14] The availability of such detailed information is of considerable importance in understanding the origins of chiral induction in the reaction. A preliminary summary of part of this work has appeared previously.[15]

Experimental Details

The preparation of $K_3[Co(ox)_3]\cdot 3.5H_2O$ (ϵ_{605} = 165 M^{-1} cm^{-1}) and resolution of the complex were carried out by literature methods.[16,17] The absolute configuration is taken as Λ-$(-)_{589}$-$[Co(ox)_3]^{3-}$ ($\Delta\epsilon_{622}$ = 3.80 M^{-1} cm^{-1}).[18] The complex is sensitive to heat and light, and all manipulations were carried out in subdued light. Racemization of the complex amounts to 10–12% over a 2-h period, and where applicable, this was applied as a correction factor in the studies.

For the kinetic experiments, horse heart cytochrome *c* (Sigma, Type VI) was purified by chromatography on Whatman carboxymethylcellulose cation-exchange resin before use.[19] However, stereoselectivity experiments involving product analysis use substantial amounts of the protein and in these instances Sigma Type VI was used without further purification. Samples of the protein were dialyzed in appropriate buffer solutions for at least 2 h before use. The reduced protein was obtained by the addition of a few crystals of sodium dithionite to the oxidized protein followed by dialysis with argon-saturated buffer under an atmosphere of argon.

Electron-transfer stereoselectivities were determined by two independent methods. Experiments to measure optical activity induced in $[Co(ox)_3]^{3-}$ on reaction with cytochrome *c* were carried out by mixing 5 mL of 3 × 10^{-4} M cyt *c* in appropriate buffer and ionic strength with equal volumes containing a 2–17-fold excess of $[Co(ox)_3]^{3-}$, also in buffer at 23 °C. After the reaction was allowed to proceed to completion, the protein was removed on Sephadex SP C-25 resin and the optical activity in the remaining $[Co(ox)_3]^{3-}$ determined. In other experiments, the difference in reactivity was measured directly with use of a Hewlet Packard 8452 diode-array spectrophotometer equipped with a 300-nm cut-off filter and with appropriate precautions to avoid photochemical degradation. Kinetic measurements were made at 550 nm under pseudo-first-order conditions with either Δ- or Λ-$[Co(ox)_3]^{3-}$ at concentrations in the range (1.54–1.69) × 10^{-3} M, which was at least 100-fold excess over the protein concentration. A 0.214 M phosphate buffer, pH 7.0, was used to give an ionic strength of 0.50 M at 25.0 °C.

Equilibrium dialysis experiments were carried out with 5 mL of ≈ 5 × 10^{-4} M reduced cyt *c* in 0.214 M phosphate buffer, pH 7.0, dialyzed against 5 mL of 1.5 × 10^{-3} M racemic $[Cr(ox)_3]^{3-}$ in the same buffer for 1 h at 25 °C. The $[Cr(ox)_3]^{3-}$ solution was then examined for optical activity.

Table I. Rate Constants for the Oxidation of Cytochrome *c* by Δ- and Λ-$[Co(ox)_3]^{3-}$ at 25.0 °C, pH 7.0, and Ionic Strength 0.50 M (Phosphate)

$10^3[[Co(ox)_3]^{3-}]$, M	enantiomer	10^3k_{obsd}, s^{-1}	k, M^{-1} s^{-1}
1.62	Δ	6.70 (0.01)	4.13
1.62	Δ	7.07 (0.03)	4.35
1.62	Δ	6.89 (0.01)	4.25
1.62	Δ	7.11 (0.08)	4.39
1.69	Λ	8.31 (0.01)	4.92
1.69	Λ	8.23 (0.01)	4.87
1.54	Λ	7.20 (0.01)	4.67
1.54	Λ	7.33 (0.01)	4.76
1.54	Λ	7.42 (0.05)	4.82

Table II. Stereoselectivity in the Oxidation of Horse Cytochrome *c* by $[Co(ox)_3]^{3-}$ at 23 °C

pH	ionic strength, M	10^4[cyt], M	$10^4[[Co(ox)_3]^{3-}]$, M	% ee[a]	k_Δ/k_Δ
4.45	0.1[b]	2.4	5.4	5.7 (0.2)	1.121 (0.003)
6.85	0.1[c]	1.9	6.0	7.1 (0.5)	1.153 (0.007)
6.75	0.1[d]	2.1	6.5	7.9 (0.2)	1.172 (0.003)
7.00	0.1[d]	2.2	4.9	6.2 (0.3)	1.132 (0.004)
7.00	0.1[e]	2.4	4.9	4.9 (0.2)	1.103 (0.003)
7.00	0.1[c]	1.9	5.8	8.3 (0.3)	1.181 (0.004)
6.80	0.1[d]	1.4	15.1	10.0 (0.3)	1.222 (0.004)
7.00	0.25[e]	2.1	6.1	5.3 (0.5)	1.112 (0.007)
6.95	0.25[f]	1.2	10.7	6.6 (0.3)	1.142 (0.004)
7.00	0.5[g]	2.0	7.2	4.0 (0.3)	1.083 (0.004)
7.00	0.5[h]	1.7	6.8	4.3 (0.3)	1.090 (0.004)
7.00	0.5[i]	1.3	22.5	5.5 (0.6)	1.116 (0.008)
7.00	0.5[g]	1.6	4.0	2.9 (0.4)	1.060 (0.006)
7.00	0.5[g]	1.3	5.1	4.6 (0.5)	1.096 (0.007)

[a] % enantiomeric excess. [b] 5 × 10^{-3} M acetate buffer, chloride media. [c] 5 × 10^{-3} M HEPES buffer, chloride media. [d] 1.7 × 10^{-3} M phosphate buffer. [e] 1.07 × 10^{-1} M HEPES buffer, chloride media. [f] 3.0 × 10^{-2} M HEPES buffer, chloride media. [g] 2.14 × 10^{-1} M phosphate buffer. [h] 2.14 × 10^{-1} M HEPES buffer, chloride media. [i] 5 × 10^{-3} M HEPES buffer, chloride media.

Results

The kinetics and mechanism of oxidation of horse cytochrome *c* by $[Co(ox)_3]^{3-}$ have been investigated previously.[11,12,15] The reaction rate shows a first-order dependence on both [cyt *c*] and $[[Co(ox)_3]^{3-}]$ concentrations, and the second-order rate constant is independent of pH over the range 4.5–7.5 but shows a small inhibition by phosphate ion.[12,15] At pH 7.0 and 0.5 M ionic strength in phosphate buffer, with racemic oxidant, the second-order rate constant is measured to be 4.5 M^{-1} s^{-1} in satisfactory agreement with the value of 5.5 M^{-1} s^{-1} reported in the literature.[11]

Under the conditions of 0.5 M ionic strength, pH 7.0, the enantiomeric forms of $[Co(ox)_3]^{3-}$ react at measurably different rates with cytochrome *c*. However, since the enantiomeric differences are small, only very precise rate measurements allow direct detection of these differences. The principal source of uncertainty in the kinetic measurements is the determination of the exact concentration of $[Co(ox)_3]^{3-}$, because this complex is both thermally and photochemically decomposed over times relevant to kinetic measurements. Moreover, decomposition

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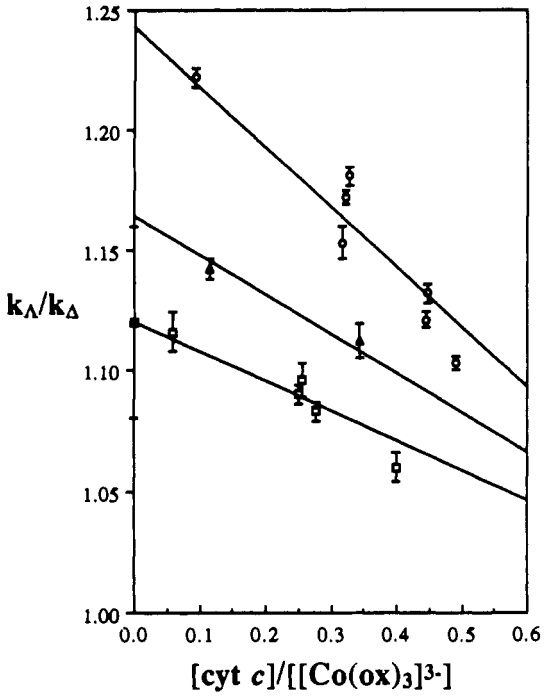

Figure 1. Plot of k_Λ/k_Δ determined from product analysis experiments against [cyt *c*]/[$[Co(ox)_3]^{3-}$] for the reduction of $[Co(ox)_3]^{3-}$ by cytochrome *c* at ionic strength 0.10 M (circles), 0.25 M (triangles), and 0.50 M (squares). The value obtained from the kinetic experiment is shown at the intercept of the 0.50 M data.

products catalyze racemization of the complex. To minimize these effects, only freshly prepared $[Co(ox)_3]^{3-}$ was used and all work was done in subdued light. In addition, reactions were carried out with a 100-fold or greater stoichiometric excess of the cobalt complex and stock solutions were analyzed spectrophotometrically before and after reaction. During kinetic measurements a 300-nm filter was used to eliminate exposure of the sample to higher energy light, and the spectrophotometer was programmed to read absorbances no more frequently than 40 times per kinetic run and then only for 0.1-s exposure for each reading. This approach allowed the acquisition of very precise kinetic data for the oxidation of cyt *c* by Λ- and Δ-$[Co(ox)_3]^{3-}$, respectively, and observed rate constants for individual experiments are collected in Table I. The mean second-order rate constants are k_Λ = 4.81 (0.10) M^{-1} s^{-1} and k_Δ = 4.28 (0.12) M^{-1} s^{-1}.

Reduction of a solution containing an excess of racemic $[Co(ox)_3]^{3-}$ results in the preferential reduction of the Λ isomer such that an enantiomeric excess of Δ-$[Co(ox)_3]^{3-}$ remains. For example, the circular dichroism spectrum of the $[Co(ox)_3]^{3-}$ remaining after reaction of 7.2 × 10^{-4} M $[Co(ox)_3]^{3-}$ with 2.0 × 10^{-4} M cyt *c* in phosphate buffer at 0.50 M ionic strength shows a negative signal at 600 nm with $\Delta\epsilon_{app}$ = 0.041 M^{-1} cm^{-1} (app = apparent). Thus, the measured enantiomeric excess for the $[Co(ox)_3]^{3-}$ that reacted is 4.0% Λ, which corresponds to an apparent rate ratio of 1.083. Values measured under a variety of conditions are presented in Table II. Since consumption of the faster reacting Λ-$[Co(ox)_3]^{3-}$ leads to a relative excess of the slower reacting Δ-$[Co(ox)_3]^{3-}$ in the reaction mixture, the stereoselectivity measured in the unreacted oxidant shows a dependence on the excess of $[Co(ox)_3]^{3-}$ used in the reaction.[20] The value of k_Λ/k_Δ can be corrected by extrapolation of the rate ratio to an infinite excess of $[Co(ox)_3]^{3-}$ (Figure 1), and the limiting value is 1.12 in good agreement with the value from the kinetic experiments.

The stereoselectivity has been examined as a function of pH and buffer and is found to be insensitive to both. In particular, phosphate ion, which shows a small inhibitory effect on the reaction rate, has no measurable effect on the stereoselectivity and must affect k_Δ to the same extent as k_Λ. There is, however, a pronounced dependence on ionic strength, with the rate ratio, k_Λ/k_Δ, decreasing from 1.24 to 1.12 as the ionic strength increases from 0.10 to 0.50 M.

Discussion

The stereoselectivities determined by both kinetic and product analysis experiments show very good agreement with k_Λ/k_Δ = 1.12 at 25.0 °C and 0.50 M ionic strength. This value, which represents an enantiomeric excess of 6% favoring the Λ isomer, is considerably larger than the stereoselectivity noted[10] for the reaction of $[Co(acac)_3]$, 0.28% favoring the Δ isomer (15 vol % ethanol–water, 0.1 M ionic strength), and is consistent with expectations based on a stronger interaction of the negatively charged $[Co(ox)_3]^{3-}$ with the positively charged protein. In addition, the observation that there is a decrease in stereoselectivity as the ionic strength increases is best explained by a stereoselective interaction between the protein and the complex, which is electrostatic in origin.

The apparent lack of a significant pH and buffer dependence for the stereoselectivity also contrasts with the results of the reaction with $[Co(acac)_3]$.[10] Although the reaction rate is 10–20% inhibited when chloride ion is replaced by phosphate ion,[12,15] the stereoselectivity shows no measurable difference in reactions carried out in phosphate buffer at 0.50 M ionic strength and in HEPES buffer at the same ionic strength with chloride as the anion. Both chloride ion and phosphate ion are known to bind to the surface of the protein, and two specific sites of interaction for phosphate ion have been identified.[21,22] One of these, site 2, involving lysine residues 7, 25, and 27, is close to the heme edge, while the second, site 1, is more distant and involves lysines 5, 86, 87, and 88.

There is no kinetic or other mechanistic evidence for strong binding interactions of $[Co(ox)_3]^{3-}$ with cytochrome *c* during the electron-transfer process, and strong complexes are not implicated as intermediates in the reaction. Information about the interactions of $[Co(ox)_3]^{3-}$ with cytochrome *c* has been deduced from NMR experiments with the isostructural, paramagnetic probe $[Cr(ox)_3]^{3-}$. These NMR investigations reveal the location of three sites of interaction on the protein surface, at the phosphate binding sites 1 and 2 and at a third, site 3, involving lysines 13, 72, and 86, also close to the heme edge. The paramagnetic ion has a higher affinity for sites 1 and 3 than for site 2. Site 3, close to the heme edge, is thought to be kinetically more important in reactions with anionic complexes[23] and is not inhibited by phosphate. It is proposed that the source of chiral recognition is the preferential reaction of the Λ isomer of $[Co(ox)_3]^{3-}$ at this site.

Some indirect support for this mechanism can be obtained from binding studies. Although the magnitude of the binding constant between $[Cr(ox)_3]^{3-}$ and cytochrome *c* is too small to be measured directly, the site averaged stereoselectivity of the binding interaction with $[Cr(ox)_3]^{3-}$ can be probed by equilibrium dialysis experiments. When 5 × 10^{-4} M reduced horse cytochrome *c* is dialyzed against an equal volume of a solution containing 1.5 × 10^{-3} M $[Cr(ox)_3]^{3-}$, the concentration of the isomeric form that binds preferentially to the protein is depleted in the bulk solution. Detection of this chiral recognition is achieved by examining the circular dichroism spectrum of the bulk solution.[24] The spectrum

(20) In order to enhance the precision of the experiment, the ratio of [[Co(ox)$_3$]$^{3-}$]/[cyt *c*] must be as low as possible, but this introduces inaccuracies. During the course of the experiment, as Λ-$[Co(ox)_3]^{3-}$ is depleted at a rate faster than Δ-$[Co(ox)_3]^{3-}$, the oxidant will not remain a racemic mixture, and the measured value of the rate ratio will be smaller than k_Λ/k_Δ. Individual measurements can be corrected for this effect (Geselowitz, D. Ph.D. Dissertation, Stanford University, 1982; pp 22–23), but a more precise value is obtained by extrapolation.

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shows a weak signal of ≈+1 mdeg at 552 nm due to the Δ isomer, which indicates preferential binding to the protein by the Λ isomer. The experiment is difficult and the magnitude of the result is at the limits of detection; however, a similar result was obtained that indicated the selective binding of Λ-$[Co(ox)_3]^{3-}$ to the oxidized protein in a previous study.[15] Like the stereoselective electron-transfer experiment, interpretation of this chiral recognition of $[Cr(ox)_3]^{3-}$ by cytochrome *c* is difficult. Although the number of strong interactions between the protein and $[Cr(ox)_3]^{3-}$ appears limited, the stereoselectivity observed is the weighted average of all the interactions that take place. Thus, a highly stereoselective but minor interaction can make a larger contribution to the overall value than a dominant, less selective interaction. Nevertheless, it is of considerable interest to note that the chiral recognition in the binding interaction favors the same Λ isomer as chiral induction in the electron-transfer process.

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Registry No. $[Co(ox)_3]^{3-}$, 15053-34-6; Λ-$[Co(ox)_3]^{3-}$, 21826-66-4; Δ-$[Co(ox)_3]^{3-}$, 82409-68-5; cytochrome *c*, 9007-43-6.

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A Simple Synthetic Route to Platinum–Carbonyl–Phosphine Cluster Compounds

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Introduction

Transition-metal carbonyl cluster compounds have been extensively studied over the last 30 years.[1] Many of these compounds homogeneously catalyze reactions such as the hydrogenation of carbon monoxide[2] and alkenes[3] or the water gas shift reaction.[4] Of particular interest has also been the analogy between transition-metal surfaces employed in heterogeneous catalysis and cluster compounds.[5] Platinum clusters of the type $[Pt_3(\mu_2\text{-}CO)_3L_3]$ (L = bulky tertiary phosphine) (3:3:3; **1**) have also been employed as starting materials for the synthesis of heterometallic cationic species of the types $[\{Hg_2\}(3:3:3)_2]^+$,[6] $[\{LM\}(3:3:3)]^+$,[7] and $[M(3:3:3)_2]^+$[8] (L = PR_3; M = Cu, Ag, Au).

However, the application of compounds of type **1** in both homogeneous and heterogeneous catalysis has hardly been investigated to date. This may be related to the lack of availability of a systematic methodology for preparing these compounds as well as their homologues $[Pt_4(\mu_2\text{-}CO)_5L_4]$ (4:5:4; **2**). Furthermore, established methods require the use of compounds such as $[Pt(COD)_2]$ (COD = 1,5-cyclooctadiene),[9] which is not easily accessible, or of the type *trans*-$[PtHCl(PR_3)_2]$.[10] Here we report a simple preparative method for compounds of types **1** and **2**.

Experimental Section

Solvents were obtained from Fluka and used as received. Other reagents employed: $NaBH_4$, Fluka purum; $PtCl_2$, Johnson Matthey; PMe_2Ph, Fluka purum. The other ligands $P(^iPr)_3$,[11] and $PPh(^iPr)_2$,[12] $PPhCy_2$,[13] PCy_3,[14] and $PMeCy_2$[15] and the intermediates $[PtCl_2(MeCN)_2]$ (**3**)[16] and $[PtCl_2(COD)]$ (**4**)[17] were prepared by literature methods. The IR spectra were recorded on a Perkin-Elmer 1430 spectrometer, and the NMR spectra were obtained on a Bruker HX 90, WH 90, or WM 250 instrument. Elemental analyses were performed by the Microanalytical Laboratory of the ETH, Zürich.

Synthesis of the Compounds $[Pt_3(\mu_2\text{-}CO)_3L_3]$ and $[Pt_4(\mu_2\text{-}CO)_5L_4]$. General Procedure. The complex $[PtCl_2(MeCN)_2]$ (or $[PtCl_2(COD)]$) (0.2–1 g) was suspended in acetonitrile (10–50 mL). The tertiary phosphine (1 equiv) was added, and the resulting clear solution (or suspension) was stirred for 30 min while carbon monoxide was bubbled through the solution. On addition of an excess of solid $Na[BH_4]$ (ca. 5 equiv), the mixture slowly turned brown. After 20 min of stirring under a carbon monoxide atmosphere, 2–5 mL of CH_3OH was slowly added. Increased gas evolution was observed, and the mixture turned red. Stirring under a carbon monoxide atmosphere was continued for 3 h. The solvent was then removed under vacuum, and the brown residue was extracted with dichloromethane or toluene. The dark solution was filtered through Celite and concentrated under reduced pressure to a few milliliters. Addition of a large volume of CH_3OH (50–100 mL) gave, after cooling to −20 °C overnight, the product as a crystalline material. Unless otherwise noted, all compounds are air stable both in solid state and in solution.

$[Pt_3(\mu\text{-}CO)_3(P(^iPr)_3)_3]$ (1a): from **3** (1.1 g, 3.16 mmol) and P^iPr_3 (0.51 g, 3.16 mmol); yield 80%. Anal. Calcd for $C_{30}H_{63}O_3P_3Pt_3$: C, 31.34; H, 5.52. Found: C, 31.93; H, 5.50.

$[Pt_3(\mu_2\text{-}CO)_3(PPh^iPr_2)_3]$ (1b): from **3** (1 g, 2.87 mmol) and PPh^iPr_2 (0.6 g, 3.09 mmol); yield 80%. Anal. Calcd for $C_{39}H_{57}O_3P_3Pt_3$: C, 37.41; H, 4.59. Found: C, 37.54; H, 4.54.

$[Pt_3(\mu_2\text{-}CO)_3(PPhCy_2)_3]$ (1c): from **4** (0.6 g, 1.60 mmol) and $PPhCy_2$ (0.45 g, 1.64 mmol); yield 80%. Anal. Calcd for $C_{57}H_{81}O_3P_3Pt_3$: C, 45.27; H, 5.47. Found: C, 44.87; H, 5.42.

$[Pt_3(\mu_2\text{-}CO)_3(PCy_3)_3]$ (1d): from **4** (1 g, 2.67 mmol) and PCy_3 (0.75 g, 2.67 mmol); yield 65%. Anal. Calcd for $C_{57}H_{99}O_3P_3Pt_3$: C, 45.32; H, 6.61. Found: C, 45.42; H, 6.71.

$[Pt_4(\mu_2\text{-}CO)_5(PBz_3)_4]$ (2a): from **4** (0.8 g, 2.14 mmol) and PBz_3 (0.65 g, 2.14 mmol); yield 65%. Anal. Calcd for $C_{89}H_{84}O_5P_4Pt_4$: C, 50.00; H, 3.40. Found: C, 49.89; H, 4.18.

$[Pt_4(\mu_2\text{-}CO)_5(PMe_2Ph)_4]$ (2b): from **3** (1 g, 2.87 mmol) and PMe_2Ph (0.4 g, 2.90 mmol); yield 70%. Anal. Calcd for $C_{37}H_{44}O_5P_4Pt_4$: C, 30.16; H, 2.99. Found: C, 30.35; H, 3.00.

$[Pt_4(\mu_2\text{-}CO)_5(PEt_3)_4]$ (2c): from **3** (0.8 g, 2.87 mmol) and PEt_3 (0.34 g, 2.87 mmol); yield 70%. Anal. Calcd for $C_{32}H_{42}O_5P_4Pt_4$: C, 25.00; H, 4.34. Found: C, 25.11; H, 4.19.

Results and Discussion

Preparation of the Compounds $[Pt_3(\mu\text{-}CO)_3L_3]$ (L = P^iPr_3 (1a), PPh^iPr_2 (1b), $PPhCy_2$ (1c), PCy_3 (1d)) and $[Pt_4(\mu_2\text{-}CO)_5L_4]$ (L = PBz_3 (2a), PMe_2Ph (2b), PEt_3 (2c)). The preparation of compounds **1a–d** and **2b** starting from either *cis*-$[PtCl_2(PR_3)_2]$ or *trans*-$[PtHCl(PR_3)_2]$[10a] and using CO in alkaline solution as reducing agent has been previously reported. Goel and coworkers[10b] described the formation of $[PtH_2(PR_3)_2]$ starting from $[PtCl_2(COD)]$ and bulky phosphines. Reductive elimination of H_2, in the presence of CO, gave the $[Pt_3(\mu_2\text{-}CO)_3(PR_3)]$ clusters. We find that this rather cumbersome procedure can be avoided

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