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Crystal Structure and Coordination Chemistry of the Pentane-Soluble Sodium Salt of an Oxygen Tripod Ligand

W. Kläui,*[†] A. Müller,[†] W. Eberspach,[†] R. Boese,*[‡] and I. Goldberg[§]

Contribution from the Institut für Anorganische Chemie der Technischen Hochschule Aachen, D-5100 Aachen, FRG, the Institut für Anorganische Chemie der Universität Essen, D-4300 Essen, FRG, and the School of Chemistry, Tel Aviv University, 69978 Ramat Aviv, Israel. *Received July 14, 1986*

Abstract: The sodium salt of the anionic halfsandwich complex $[C_5H_5Co\{P(O)(OC_2H_5)_2\}_3]^- \equiv L^-$ crystallizes as trimeric aggregate $(NaL)_3{\cdot}2H_2O$. Crystal data are as follows: a = 10.866 (2) Å, b = 25.048 (4) Å, c = 31.378 (9) Å, β = 98.77 (2)°, Z = 4, d_{calcd} = 1.35 g cm^{-3}, and space group $P2_1/c$. The complex anion L^- reacts as an oxygen tripod ligand with $M(CO)_6$ to form $[LM(CO)_3]^-$ (**1a**, M = Mo, **1b**, M = W). **1a** reacts with allyl iodide to give $[LMo(CO)_2(\eta^3\text{-}C_3H_5)]$. The hydride complexes $[LM(CO)_3H]$ (**2a,b**), obtained by protonation of **1a,b**, undergo insertion reactions with isoprene to give the allyl complexes $[LM(CO)_2(\eta^3\text{-}C_5H_9)]$. **2b** can be halogenated to give $[LW(CO)_3X]$, X = Cl, Br, and I. **2b** is oxidized by air to yield the tungsten oxo complex $L_2W_2O_6$. The ML_2 complexes $[V(O)L_2]$, $[VL_2]PF_6$, $[CrL_2]PF_6$, $[TiL_2]PF_6$, and $[TiL_2](PF_6)_2$ have been prepared from the reaction of NaL in water or tetrahydrofuran with oxovanadium(IV), vanadium(III), chromium(III), and titanium(III) salts. The mixed ligand complexes $[LSnCl_3]$, $[LZrCl_3]$, $[LMo(O)Cl_2]$, $PPh_4[LRhCl_3]$, and $[\{LRhCl_2\}_2]$ have been synthesized likewise.

We have recently described the synthesis[1] of the organometallic cobalt complex $[C_5H_5Co\{P(O)(OC_2H_5)_2\}_3]^-$ (Figure 1). This anionic halfsandwich complex has virtually no[2] chemistry other than being an oxygen tripod ligand using its three P=O oxygen atoms as donor centers.

The coordination chemistry of this ligand (hereafter abbreviated as L^-) is remarkably many-sided. It forms very stable 2:1 complexes ML_2 with M = Mn^{2+}–Zn^{2+}, the alkaline-earth metal ions Mg^{2+}–Ba^{2+}, and ML_2^+ with the earth metal ions Al^{3+}–Tl^{3+} and the lanthanides Ln^{3+} as expected for a tris-chelating oxygen ligand.[1,3] We have characterized L^- by ligand field spectroscopy as a very hard and weak oxygen ligand, comparable with the hydroxide and fluoride ions.[4] From this characterization we expected a distinct preference of L^- for metal ions in high oxidation states. In contrast to this we found that L^- can stabilize many low-valent organometallic fragments like $[Rh(C_2H_4)_2]^+$[5] or $[W(CO)_3H]^+$.[6] When we studied the organometallic chemistry of the oxygen tripod ligand, we could make use of the remarkable property that the alkali-metal salts ML are soluble in water as well as in pentane. The stability constant of the sodium 1:1 complex turned out to be higher than that of all sodium crown ether complexes known so far.[7] The sodium salt crystallizes as hydrate from aqueous solutions. Thermogravimetric measurements show the loss of 1 mol of water per mole of NaL in the temperature range +20 to +100 °C in dry nitrogen. From osmometric molecular weight determinations, we learned that NaL hydrate forms trimeric units in noncoordinating solvents (found M_r = 1650 in benzene, calculated 1728 for $(NaL{\cdot}H_2O)_3$). Dry NaL shows the same molecular weight (found 1700 in benzene, calculated 1674 for $(NaL)_3$). Several attempts to grow crystals from different solvents did not yield single crystals suitable for an X-ray structure determination. It was interesting to note however that all crystals contained three molecules of NaL in the smallest asymmetric unit. We have now grown appropriate single crystals from acetone. In this paper we describe first its crystal structure and then some representative coordination chemistry of NaL, inter alia a reaction sequence which shows that an oxygen tripod ligand–tungsten unit stays intact, while tungsten is oxidized from W(0) to W(VI).

Crystal Structure

The sodium salt of the oxygen tripod ligand, NaL, forms a trimeric aggregate depicted in Figure 2. The sodium triangle with Na–Na distances of 3.277 (7) Å (Na1–Na2), 3.431 (7) Å (Na1–Na3), and 3.290 (8) Å (Na2–Na3) is asymmetrically bicapped by the oxygen atoms of two water molecules (O28, O29). Each sodium atom is moreover coordinated to three oxygen donor atoms of the tripod ligands: one of them bridging two sodium atoms, the second standing axial, and the third standing equatorial to the triangle. With respect to the sodium triangle, two axial oxygen atoms are pointing in the same direction (O7 and O25) and one in the opposite direction (O16) (see Figure 3). Referred to the oxygens only, the sodium atoms are surrounded by a distorted octahedron.

The lack of any symmetry seems to arise from the fact that alternating axial positioning of oxygen atoms is not possible at a triangle. This gives a high variation in bond lengths (Na–O) and angles (O–Na–O) but still there is a trend of Na–O (axial) to be shorter than Na–O (bridging) and to be shorter than Na–O (equatorial) (2.28, 2.34, and 2.36 Å, mean values). The same is reflected in P–O bond lengths with P–O (axial) to be shorter than P–O (bridging) to be shorter than P–O (equatorial) (1.47, 1.49, and 1.50 Å, mean values). The $P\text{–}OC_2H_5$ distances are in the normal range of 1.62 Å, mean value, as are the Co–P and Co–C (cyclopentadienyl rings) distances (2.17 and 2.086 Å, respectively, mean values).

The "bite" of the ligand L^-, i.e., the nonbonding O···O distance of the oxygen donor atoms, varies from 3.00 to 3.28 Å. The nonbonding O···O distances of O (axial) to O (bridging) are shorter than the O (equatorial)···O (axial) and shorter than O (equatorial)···O (bridging) (3.05, 3.25, and 3.26 Å, mean values). These values demonstrate the flexibility of the facially coordinating oxygen tripod ligand with respect to the possibility to adjust to the coordination geometry of a metal.[8]

There are two more water molecules in the asymmetric unit (O30, O31; see Table I). They seem isolated, though it cannot be excluded that there are some hydrogen bridges to neighboring oxygen atoms. The hydrogen atoms could not be detected in the final difference Fourier map.

[†] Technische Hochschule Aachen.
[‡] Universität Essen.
[§] Tel Aviv University.

[1] Kläui, W. *Z. Naturforsch., B.: Anorg. Chem., Org. Chem.* **1979**, *34b*, 1403–1407.

[2] This cobalt complex is extremely robust. It is not hydrolyzed by water or concentrated sulfuric acid nor is it oxidized by air or nitric acid.

[3] Kläui, W.; Dehnicke, K. *Chem. Ber.* **1978**, *111*, 451–468.

[4] Kläui, W.; Otto, H.; Eberspach, W.; Buchholz, E. *Chem. Ber.* **1982**, 115, 1922–1933.

[5] Scotti, M.; Valderrama, M.; Rojas, S.; Kläui, W. *J. Organomet. Chem.* **1986**, *301*, 369–374.

[6] Alt, H. G.; Engelhardt, H. E.; Kläui, W.; Müller, A. submitted for publication in *J. Organomet. Chem.*

[7] Anderegg, G.; Kläui, W. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1981**, *36b*, 949–951.

[8] The "bite" of the ligand L^- is even more adjustable to the steric requirements of the metal. Nonbonding O···O distances as small as 2.8 Å have been observed.

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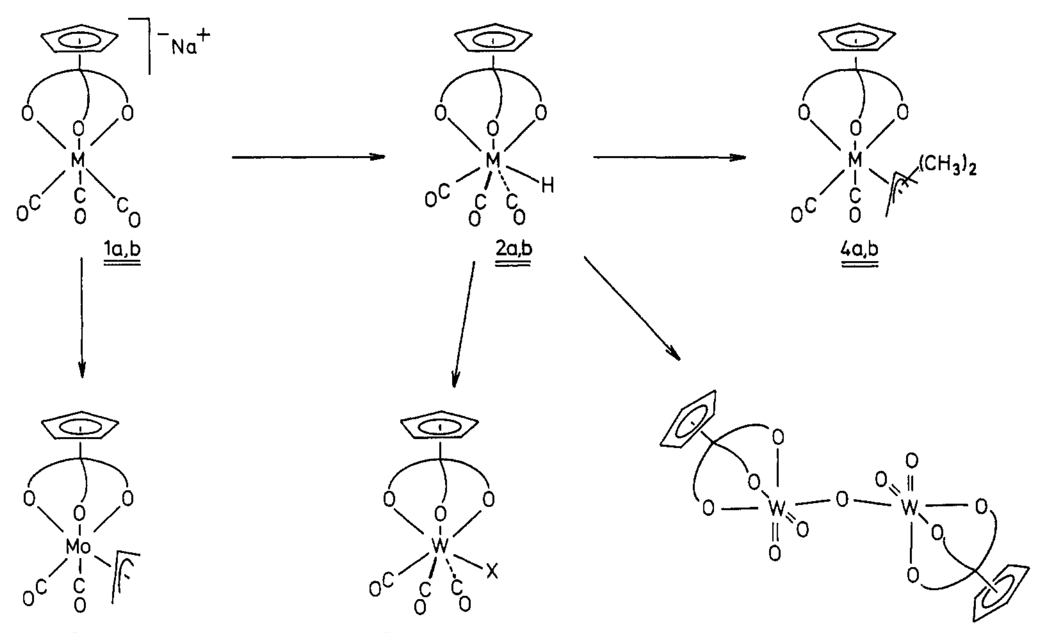
Scheme I. Schematic Reaction Sequence for the Preparation of **3–8**^{a}



^{a}**a**, M = Mo; **b**, M = W.

This crystal structure determination shows that the compound originally described as NaL·H_2O on the basis of elemental analyses and thermogravimetric measurements has in fact the composition NaL·$1^1/_3H_2O$, i.e., $(NaL)_3$·$4H_2O$. It is tempting therefore to assume that "dry" NaL still contains the triply bridging water ligands although we have no unequivocal proof of this. We have not been able to grow single crystals of anhydrous NaL. We have always obtained crystals of either the hydrated form or noncrystalline material.

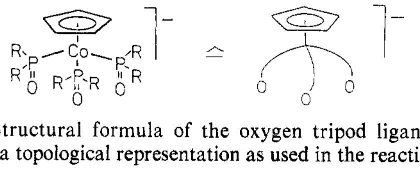


Figure 1. Structural formula of the oxygen tripod ligand L^- (R = OC_2H_5) and a topological representation as used in the reaction Schemes I and II.

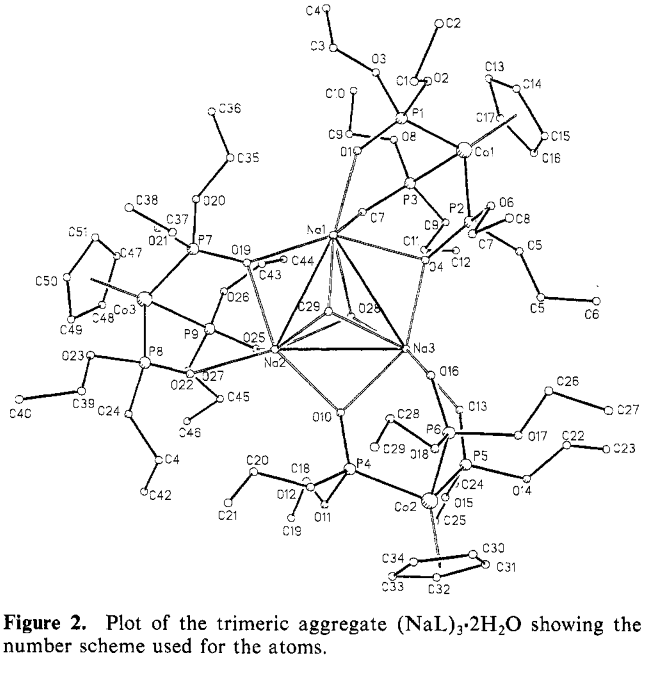


Figure 2. Plot of the trimeric aggregate $(NaL)_3$·$2H_2O$ showing the number scheme used for the atoms.

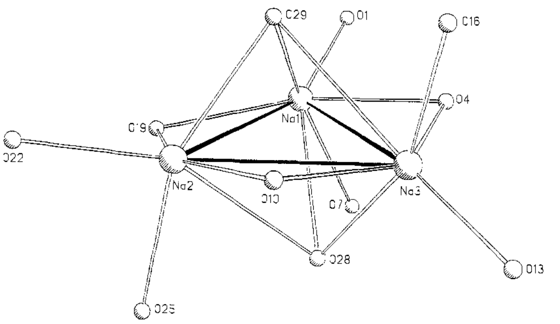


Figure 3. Sodium oxygen skeleton of $(NaL)_3$·$2H_2O$ showing the distorted octahedral NaO_6 coordination geometry.

Coordination Chemistry of L⁻. The sodium salt NaL reacts with $(CH_3CN)_3M(CO)_3$, M = Mo and W, and $(DMF)_3W(CO)_3$ in water, methanol, tetrahydrofuran, or dichloromethane to give dark-red solutions of Na[$LM(CO)_3$] (**1**). The yellow hydride complexes [$LM(CO)_3H$] (**2**) form upon addition of acetic acid to such solutions. **1** and **2** are useful starting materials for a variety of reactions as shown in Scheme I. The products **3–7** are interesting compounds since no other oxygen ligands are known to stabilize the organometallic fragments $M(CO)_2(allyl)^+$ and $M(CO)_3X^+$ (M = Mo, W; X = Cl, Br, I). The reaction of Na[$LMo(CO)_3$] (**1a**) with allyl iodide to give the η^3-allyl complex **3a** proceeds at room temperature in tetrahydrofuran within a few seconds. This is surprising in view of the fact that the analogous reaction with $[C_5H_5Mo(CO)_3]^-$ yields the σ-allyl complex $[C_5H_5Mo(CO)_3(\eta^1\text{-}C_3H_5)]$. The second step, the formation of the π-allyl complex $[C_5H_5Mo(CO)_2(\eta^3\text{-}C_3H_5)]$, proceeds only photochemically.[9,10] The reaction of the hydride complexes (**2a,b**) with isoprene gives the dimethylallyl complexes [$LM(CO)_2(\eta^3$-

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(9) Cousins, M.; Green, M. L. H. *J. Chem. Soc.* **1963**, 889–894.

(10) We anticipated higher activation energy for CO substitution in the oxygen tripod complex since the CO stretching frequencies of $PPh_4[LMo(CO)_3]$ (ν(CO) = 1886, 1729 cm^{-1} (CH_2Cl_2)[11]) and of $PMe_4[C_5H_5Mo(CO)_3]$ (ν(CO) = 1898, 1760 cm^{-1} (Nujol)[12]) suggest stronger Mo–CO bonds in the oxygen tripod ligand–molybdenum complex. It could, however, well be that the rate-determining step on going from the η^1-allyl to the η^3-allyl complex corresponds to going from the trihapto to the dihapto bonding mode of the ligand L^- and that the activation energy of this process is lower than that of the corresponding η^5 to η^3 "slipping" reaction of the cyclopentadienyl ring.

(11) Kläui, W.; Müller, A.; Scotti, M. *J. Organomet. Chem.* **1983**, *253*, 45–52.

(12) Malisch, W. *Angew. Chem.* **1973**, *85*, 228–229.

Table I. Atomic Coordinates (×10⁴) and Isotropic Thermal Parameters (Å² × 10³)

	x	y	z	U^e		x	y	z	U^e
Co1	2266 (2)	6137 (1)	2293 (1)	70 (1)*	C6	−280 (25)	7694 (11)	2791 (9)	197 (11)
Co2	133 (2)	9481 (1)	1188 (1)	64 (1)*	C7	3938 (16)	7714 (7)	2417 (6)	108 (5)
Co3	2557 (2)	6763 (1)	−576 (1)	89 (1)*	C8	4714 (21)	7916 (9)	2803 (7)	156 (8)
P1	4035 (4)	6092 (2)	2060 (1)	86 (2)*	C9	1228 (18)	5046 (8)	1215 (7)	132 (7)
P2	2127 (4)	6994 (2)	2198 (1)	72 (2)*	C10	1280 (25)	4488 (11)	1327 (9)	193 (11)
P3	1228 (4)	5975 (2)	1663 (1)	81 (2)*	C11	−1193 (36)	6110 (14)	1358 (11)	253 (15)
P4	677 (4)	9005 (1)	670 (1)	65 (1)*	C12	−2317 (27)	5902 (12)	1493 (9)	203 (11)
P5	−1157 (4)	8885 (2)	1358 (1)	73 (2)*	C13	2577 (11)	5444 (4)	2658 (4)	109 (6)
P6	1673 (4)	9182 (2)	1649 (1)	73 (2)*	C14	3096	5882	2913	96 (5)
P7	3521 (4)	6657 (2)	81 (1)	85 (2)*	C15	2126	6252	2945	101 (5)
P8	2826 (4)	7627 (2)	−569 (1)	91 (2)*	C16	1007	6044	2711	100 (5)
P9	765 (4)	6837 (2)	−358 (1)	89 (2)*	C17	1286	5544	2534	109 (6)
O1	4329 (9)	6414 (4)	1698 (3)	88 (3)	C18	−950 (18)	8584 (8)	32 (6)	120 (6)
O2	5121 (15)	6146 (7)	2464 (5)	179 (6)	C19	−1960 (21)	8714 (9)	−312 (8)	155 (8)
O3	4225 (16)	5466 (7)	1948 (6)	186 (7)	C20	2515 (15)	9185 (7)	192 (5)	103 (5)
O4	2046 (8)	7248 (3)	1772 (3)	71 (2)	C21	3295 (17)	9639 (8)	98 (6)	118 (6)
O5	929 (12)	7165 (5)	2405 (4)	137 (4)	C22	−1639 (20)	8882 (9)	2145 (7)	140 (7)
O6	3260 (11)	7250 (5)	2522 (4)	126 (4)	C23	−2752 (25)	8798 (11)	2333 (9)	188 (10)
O7	1493 (8)	6226 (3)	1248 (3)	73 (2)	C24	−3348 (20)	8543 (8)	946 (7)	131 (7)
O8	1229 (14)	5332 (6)	1595 (5)	166 (5)	C25	−4291 (21)	8699 (9)	590 (8)	154 (8)
O9	−292 (13)	6126 (6)	1701 (5)	162 (5)	C26	2020 (18)	9143 (8)	2504 (7)	131 (7)
O10	1069 (8)	8431 (3)	726 (3)	73 (2)	C27	1507 (21)	9406 (9)	2852 (7)	153 (8)
O11	−392 (9)	9051 (4)	249 (4)	102 (3)	C28	3902 (21)	9421 (10)	1532 (7)	154 (8)
O12	1792 (10)	9353 (4)	509 (4)	105 (3)	C29	4746 (26)	9883 (12)	1508 (9)	200 (11)
O13	−793 (8)	8321 (4)	1441 (3)	75 (3)	C30	343 (10)	10230 (5)	1476 (3)	100 (5)
O14	−1860 (10)	9079 (5)	1738 (4)	113 (4)	C31	−939	10093	1391	98 (5)
O15	−2340 (11)	8905 (5)	979 (4)	119 (4)	C32	−1266	10016	940	94 (5)
O16	2149 (8)	8619 (4)	1652 (3)	80 (3)	C33	−186	10106	746	92 (5)
O17	1267 (11)	9326 (5)	2120 (4)	120 (4)	C34	808	10238	1077	88 (5)
O18	2811 (11)	9593 (5)	1673 (4)	129 (4)	C35	3872 (20)	5778 (9)	556 (7)	144 (7)
O19	3162 (8)	6928 (4)	463 (3)	78 (3)	C36	4129 (27)	5184 (12)	490 (10)	214 (12)
O20	3502 (12)	6030 (5)	150 (4)	138 (4)	C37	5674 (22)	7108 (10)	323 (8)	165 (9)
O21	4973 (13)	6750 (5)	70 (4)	138 (4)	C38	6978 (30)	7104 (13)	241 (10)	230 (13)
O22	2881 (9)	7946 (4)	−179 (3)	96 (3)	C39	4697 (23)	8290 (10)	−740 (8)	167 (9)
O23	4093 (12)	7725 (5)	−776 (4)	136 (4)	C40	5249 (25)	8326 (11)	−1150 (10)	187 (10)
O24	1820 (11)	7884 (5)	−951 (4)	132 (4)	C41	977 (21)	8316 (9)	−886 (7)	156 (8)
O25	535 (8)	7204 (4)	−4 (3)	82 (3)	C42	−54 (18)	8359 (8)	−1249 (7)	132 (7)
O26	279 (12)	6258 (5)	−278 (4)	135 (4)	C43	292 (20)	6065 (9)	106 (7)	151 (8)
O27	−247 (12)	6969 (5)	−791 (4)	133 (4)	C44	−886 (24)	5718 (11)	118 (9)	187 (10)
O28	507 (8)	7175 (4)	858 (3)	79 (3)	C45	−1506 (19)	7090 (8)	−748 (7)	135 (7)
O29	3460 (8)	7917 (4)	1126 (3)	78 (3)	C46	−2258 (25)	7036 (11)	−1221 (9)	192 (11)
Na1	2973 (5)	6880 (2)	1193 (2)	76 (2)*	C47	2306 (14)	5996 (5)	−845 (4)	126 (6)
Na2	2118 (5)	7754 (2)	428 (2)	75 (2)*	C48	1724	6384	−1139	129 (7)
Na3	1003 (5)	7912 (2)	1337 (2)	69 (2)*	C49	2657	6742	−1235	114 (6)
C1	6183 (22)	6480 (10)	2490 (8)	162 (8)	C50	3815	6576	−1000	133 (7)
C2	7027 (26)	6222 (12)	2869 (9)	197 (11)	C51	3598	6114	−759	135 (7)
C3	4968 (24)	5239 (11)	1738 (8)	176 (10)	O30	5563 (10)	7346 (5)	1514 (4)	116 (4)
C4	4853 (21)	4632 (11)	1722 (8)	164 (9)	O31	8034 (17)	7402 (8)	1420 (7)	224 (8)
C5	509 (25)	7668 (11)	2442 (9)	199 (11)					

[a] The * indicates equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

C_5H_9)] (**4a,b**). This is an insertion reaction of a butadiene into a metal–hydride bond which has no counterpart in the analogous cyclopentadienyl chemistry. The complexes [$C_5H_5M(CO)_3H$] react with conjugated dienes via hydrogenation of the olefins and formation of the dimers [{$C_5H_5M(CO)_3$}$_2$].[13] The hydride complex [$LW(CO)_3H$] (**2b**) reacts with equimolar amounts of iodine or CHI_3 to give the iodide complex [$LW(CO)_3I$] (**5b**). The analogous bromide and chloride complexes **6b** and **7b** can be obtained from the reaction of **2b** with bromoform and carbon tetrachloride.

The ^1H NMR spectra of the oxygen tripod ligand in complexes **3** and **4** are distinctly different from that in **5**. The NMR spectra show that the tricarbonyl iodide fragment is fluxional on the NMR time scale. This is evident from the CH_2 signal of the six OC_2H_5 groups in L. The methylene protons give rise to one symmetrical multiplet[14] only in complexes with C_{3v} symmetry where all six OC_2H_5 substitutions are isochronous. In the compounds **3**–**7**, the symmetry is reduced to C_s or lower. Therefore, at least three different groups of methylene signals are expected. In the spectra of allyl complexes **3** and **4**, the low symmetry leads indeed to an unsymmetric nonresolved multiplet due to overlapping OCH_2 signals. The ^1H NMR spectrum of the tricarbonyl iodide complex **5b** shows, however, a symmetrical OCH_2 multiplet. We postulate that a rapid permutation of the iodide and carbonyl ligands leads to a time-averaged C_{3v} symmetry. This kind of nonrigidity is common in four-legged piano-stool complexes,[15] and we have observed this in the hydride complex **2b** as well.[6]

The tungsten(0) complex **1b** can be oxidized to give the tungsten(VI) compound **8b** for which we propose the structure as shown in Scheme I. The slow oxidation of the hydride **2b** by air is a convenient high yield route to **8b**. This reaction demonstrates that the highly inert oxygen ligand L^- tolerates metals in high oxidation states as well as low-valent organometallic fragments. In view of the spin crossover behavior of [$Co^{III}L_2$]$^+$ [16] and the ligand field spectroscopic characterization of L^- as a weak and very hard oxygen ligand,[4] it is not surprising that L^- is able to stabilize high oxidation states. We have prepared many complexes of L^- with metal ions in medium-to-high oxidation states.

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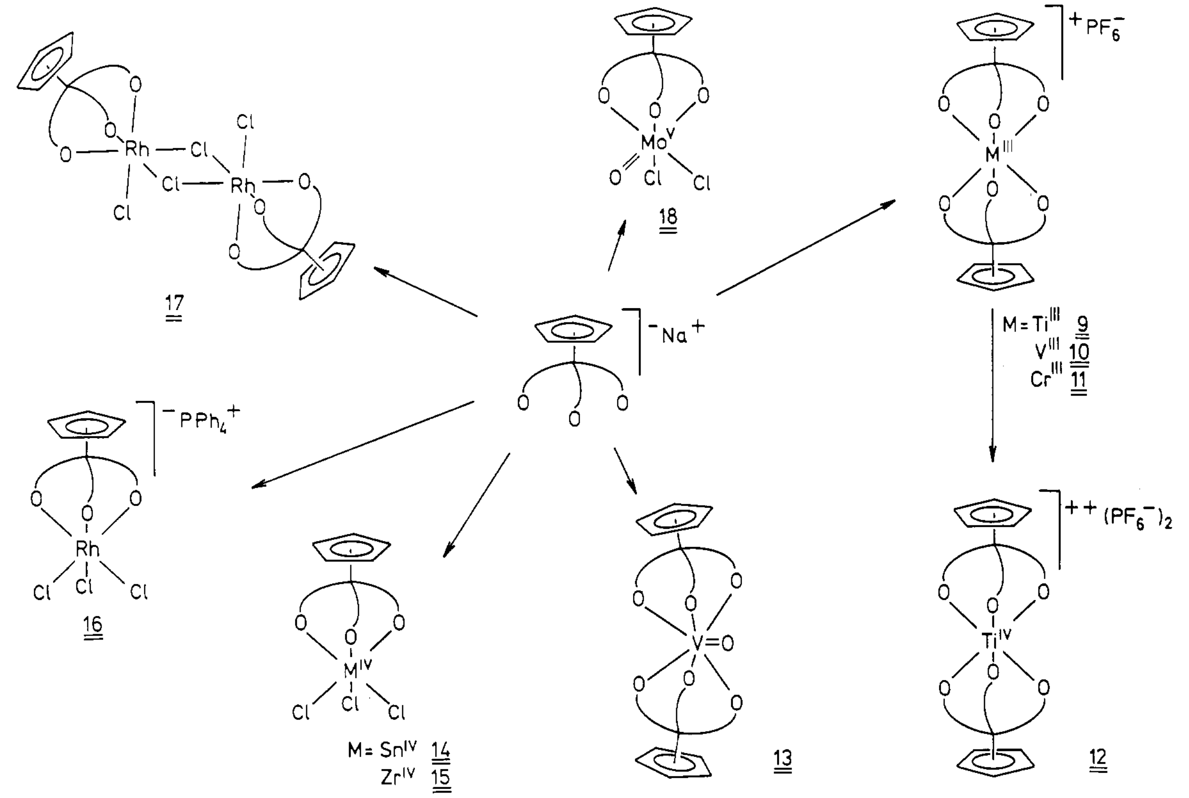
(13) Miyake, A.; Kondo, H. *Angew. Chem.* **1968**, *80*, 663–664 and 968.

(14) Thirteen lines, intensity ratio ca. 1:1:1:3:3:3:4:3:3:3:1:1:1 due to "virtual" phosphorus–proton coupling and proton–proton coupling with ^3J(POCH) ≈ ^3J(HCCH) = 7 Hz.

(15) Kubáček, P.; Hoffmann, R.; Havlas, Z. *Organometallics* **1982**, *1*, 180–188 and references cited therein.

(16) Eberspach, W.; El Murr, N.; Kläui, W. *Angew. Chem.* **1982**, *94*, 919–920 and references cited therein.

Scheme II. Schematic Structures of the Complexes **9–18**



The direct synthesis of $[ML_2]^{n+}$ from NaL in water is possible in those cases where substitutionally labile aqua ions $M_{aq}^{(n+2)+}$ exist. The strong tendency to form M^{IV}–oxo species prevents a one-step synthesis of $[Ti^{IV}L_2]^{2+}$ and $[V^{IV}L_2]^{2+}$. These species can be prepared, however, via chemical and/or electrochemical oxidation of the easily accessible $[M^{III}L_2]PF_6$ compounds **9** and **10** (see Scheme II and eq 1 and 2). The ligands L^- in $[TiL_2]^{2+}$ are shielding the central Ti^{IV} ion so effectively that it is stable for some time in aqueous solvents without decomposition to give TiO_2. The compounds $[M^{III}L_2]PF_6$ (**9–11**) are also suitable starting materials for the electrochemical reduction to $[M^{II}L_2]$, M = Ti^{II}, V^{II}, and Cr^{II} (see eq 1–3 and Figure 4).

$$[Ti^{II}L_2] \xrightleftharpoons{-1.56\ V} [Ti^{III}L_2]^+ \xrightleftharpoons{-0.30\ V} [Ti^{IV}L_2]^{2+} \quad (1)$$

$$[V^{II}L_2] \xrightleftharpoons{-1.54\ V} [V^{III}L_2]^+ \xrightleftharpoons{+0.94\ V} [V^{IV}L_2]^{2+} \quad (2)$$

$$[Cr^{II}L_2] \xrightleftharpoons{-1.60\ V} [Cr^{III}L_2]^+ \quad (3)$$

In eq 1–3, $E_{1/2}$ values vs. SCE are determined by CV in propylene carbonate, 0.2 M $[Bu_4N]PF_6$, at a Pt electrode with a scan rate of 100 mV s^{-1}. A peak-to-peak separation of 80 ± 5 mV was observed in all cases.

The mixed ligand compound $[LSnCl_3]$ (**14**) is accessible from NaL and $(NH_4)_2SnCl_6$ in aqueous hydrochloric acid (Scheme II). We have obtained other mixed ligand complexes from early and late 4d metal chlorides in anhydrous solvents. The reaction with $RhCl_3 \cdot xH_2O$ yields the mononuclear anion **16** and the dinuclear complex **17**, depending on the reaction conditions. We have also tried, but unsuccessfully, to synthesize the platinum(IV) compound $[LPtCl_3]$. Mixed ligand complexes of this type are very rare. The compound with the composition $PtL_2Cl_2 \cdot 4HCl$ which we obtained instead turned out to be $[LH_2]_2[PtCl_6]$, a simple salt of the doubly protonated ligand L^-.

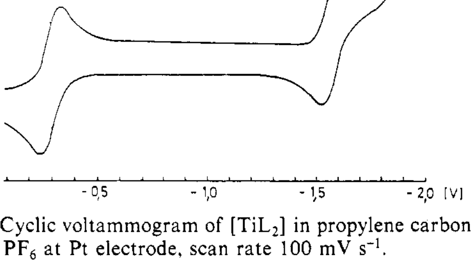


Figure 4. Cyclic voltammogram of $[TiL_2]$ in propylene carbonate: 0.2 M $[Bu_4N]PF_6$ at Pt electrode, scan rate 100 mV s^{-1}.

Concluding Remarks. This work reports the crystal structure determination of the sodium salt of an oxygen tripod ligand. We have not been able to find structurally analogous sodium salts of classical oxygen ligands. L^- seems to be the only monoanionic tris-chelating oxygen ligand with C_{3v} symmetry that has been reported so far. It is possible that the trimeric units found in the solid state resemble the species observed in noncoordinating solvents. The trimerization explains the solubility of NaL, e.g., in pentane. Our studies of the coordination chemistry of L^- reveal its unusual ability to form stable complexes with metal ions in virtually any oxidation state. The low position of L^- in the spectrochemical series[4] together with the very low CO stretching frequencies observed in the molybdenum and tungsten carbonyl derivatives characterize this ligand as a strong π-donor like the alkoxides and the oxide ion. The organometallic chemistry that we observe at the LMo and LW fragments could therefore resemble the organometallic chemistry occurring on metal oxide surfaces, e.g., the chemistry on the surfaces of metal oxide based heterogeneous catalysts.

Experimental Section

Collection and Reduction of X-ray Data. Crystals of $(C_{17}H_{35}CoNaO_9P_3)_3 \cdot 4H_2O$ have monoclinic symmetry, space group $P2_1/c$. An irregularly shaped crystal of the approximate dimensions 0.38 × 0.29 × 0.24 mm^3 was mounted on a Nicolet R3 four-circle diffractometer. Cell constants were obtained from a least-squares fit of the setting angles of 25 reflections at room temperature: $a = 10.866$ (2) Å, $b = 25.048$ (4) Å, $c = 31.378$ (9) Å, $\alpha = \gamma = 90°$, $\beta = 98.77$ (2)°, $V = 8440$ (3) Å^3, $Z = 4$, $d_{calcd} = 1.35$ g/cm^3, μ(Mo Kα, graphite monochromator) = 8.32 cm^{-1}. A total of 10947 independent unique intensities were obtained ($2\theta_{max} = 45°$), 6700 of which were regarded as observed ($F_o \geq 6.0\sigma(F)$).

Structure Solution and Refinement. The structure was solved[17] by direct methods and successive difference Fourier maps and least-squares

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(17) Sheldrick, G. M. SHELXTL, Göttingen, FRG, Revision 4.1, 1984.

cycle processes which revealed the positions of all non-hydrogen atoms. Cobalt and phosphorus atoms were given anisotropic temperature factors. All other atoms were calculated with isotropic temperature factors. Hydrogen atoms were not included because of the poor crystal quality and the disorder of ethoxy groups, which could not be resolved. Cyclopentadienyl rings were treated as rigid groups with C–C distances of 1.420 Å and C–C–C angles of 108.0°. The atomic scattering factors were those incorporated in SHELXTL.[17] All calculations were performed on a NOVA 3/12 computer, the final refinement of 437 parameters converged to $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.113$ and $R_w = [\sum w||F_o| - |F_c||^2/\sum w|F_o|^2]^{1/2} = 0.126$, $w^{-1} = \sigma(F_0)^2(4 \times 10^{-4}F_0^2)$, and the maximum residual electron density was 1.4 e/Å^3 at a distance of 1.5 Å from P3.

Reagents and General Techniques. All reactions were performed under dry nitrogen in conventional Schlenk glassware. Infrared spectra were recorded on a Perkin-Elmer PE 580 spectrometer. ^{1}H and ^{13}C NMR spectra were obtained on a Bruker WP80 or Bruker WH270 NMR spectrometer. Electron-impact (70-eV) mass spectra were run on a Varian MAT CH5 spectrometer. Cyclovoltammograms were obtained with a PAR potentiostat, Model 173. Microanalyses and osmometric molecular weight determinations were performed by Malissa and Reuter, Analytical Laboratories, Engelskirchen, FRG. The compounds VCl_3,[18] $CrCl_3 \cdot 3THF$,[19] **2a**,[11] **2b**,[6] $MoCl_4(CH_3CN)_2$,[20] and NaL[1] were prepared by literature methods.

Preparations. [(Cyclopentadienyl)tris(diethylphosphito-*P*)cobalt-*O*,*O′*,*O″*](η^3-allyl)dicarbonylmolybdenum (3a). A suspension of 1.12 g (2 mmol) of NaL and 528 mg (2 mmol) of $Mo(CO)_6$ in acetonitrile was heated to reflux. After 4 h the solvent was removed in vacuo and replaced by tetrahydrofuran. To the resulting dark-red solution of **1a** was added 0.5 mL of allyl iodide. The solution was pumped to dryness at reduced pressure, and the light-brown residue was extracted with warm hexane. The extracted solution was concentrated to ca. 50 mL and cooled overnight to −20 °C: yield 860 mg (1.18 mmol, 59%) large yellow airstable needles. IR (KBr) ν(CO) 1921 (s), 1822 (s) cm^{-1}; ^{1}H NMR (80 MHz, CD_3COCD_3) δ 0.83 (d, 2, C_3H_5, ^3J(HCCH) = 8.6 Hz), 1.29 (t, 18, $POCH_2C\mathit{H}_3$, ^3J(HCCH) = 7.1 Hz), 2.8–3.3 (overlapping multiplets, 3, C_3H_5), 3.8–4.3 (unsym. m, br, 12, $POCH_2$), 4.94 (q, 5, C_5H_5, ^3J(PCoCH) = 0.4 Hz); ^{13}C NMR (67.88 MHz, CD_3COCD_3) δ 16.9 (q, $POCH_2\mathit{C}H_3$, ^1J(CH) = 126.9 Hz), 59.0 (tm, $\mathit{C}H_2CH\mathit{C}H_2$, ^1J(CH) = 163.6 Hz), 61.2 (t, br, $POCH_2$, ^1J(CH) = 136 Hz), 74.6 (d, $CH_2\mathit{C}HCH_2$, ^1J(CH) = 168.4 Hz), 89.8 (dm, C_5H_5, ^1J(CH) = 183.1 Hz), 231.6 (s, CO); MS (70 °C), *m/e* (relative intensity) 730 (M^+, 25%), 674 (M^+ − 2CO, 100%). Anal. Calcd for $C_{22}H_{40}CoMoO_{11}P_3$: C, 36.28; H, 5.54. Found: C, 36.08; H, 5.75.

[(Cyclopentadienyl)tris(diethylphosphito-*P*)cobalt-*O*,*O′*,*O″*](η^3-dimethylallyl)dicarbonylmolybdenum (4a).[21] To a stirred solution of 1.10 g (1.54 mmol) of **2a** in 50 mL of warm hexane was added 1 mL of isoprene. After a few seconds gas evolved, and the yellow solution became red. After 40 min the solvent was concentrated and chromatographed through a column of alumina. Dichloromethane was used to elute a yellow band. The solvent was removed at reduced pressure, and the solid residue was extracted with hot hexane. Crystallization at −20 °C afforded bunches of air-stable yellow needles (556 mg, 0.74 mmol, 48%): IR (KBr) ν(CO) 1916 (s), 1817 (s) cm^{-1}; ^{1}H NMR (80 MHz, C_6D_6) δ 1.2 (overlapping C_5H_5, and t, 21, $POCH_2C\mathit{H}_3$ and CH_3 of C_5H_9), 2.0 (m, 1, C_5H_9), 2.2 (s, 3, CH_3 of C_5H_9), 3.5 (m, 2, C_5H_9), 3.8–4.3 (unsym. m, br, 12, $POCH_2$), 4.74 (q, 5, C_5H_5, ^3J(PCoCH) = 0.5 Hz); ^{13}C NMR (67.88 MHz, CD_3COCD_3) δ 17.0 (q, $POCH_2\mathit{C}H_3$, ^1J(CH) = 126.4 Hz), 22.9 (q, CH_3 of C_5H_9, ^1J(CH) = 126.4 Hz), 25.6 (q, CH_3 of C_5H_9, ^1J(CH) = 126.4 Hz), 56.6 (t, CH_2 of C_5H_9, ^1J(CH) = 158 Hz), 61.4 (t, br, $POCH_2$, ^1J(CH) = 146 Hz), 77.1 (d, CH of C_5H_9, ^1J(CH) = 163.5 Hz), 84.3 (s, C of C_5H_9), 89.8 (dm, C_5H_5, ^1J(CH) = 180.9 Hz), 232.6 (s, CO), 234.8 (s, CO). Anal. Calcd for $C_{24}H_{44}CoMoO_{11}P_3$: C, 38.11; H, 5.86. Found: C, 38.13; H, 5.92.

[(Cyclopentadienyl)tris(diethylphosphito-*P*)cobalt-*O*,*O′*,*O″*](η^3-dimethylallyl)dicarbonyltungsten (4b).[21] This compound was prepared in the same manner as **4a** from 120 mg (0.15 mmol) of **2b** and 0.2 mL of isoprene in 10 mL of hexane. The reaction mixture was kept at room temperature for 4 days before chromatography: yield 84 mg (0.10 mmol, 67%) of yellow needles. The compound decomposed very slowly at room temperature: IR (KBr) ν(CO) 1898 (s), 1797 (s) cm^{-1}; ^{1}H NMR (80 MHz, C_6D_6) δ 1.13 (t, br, 18, $POCH_2C\mathit{H}_3$), 1.56 (s, 3, CH_3 of C_5H_9), 2.25 (s, 3, CH_3 of C_5H_9), 2.26 (d, 1, CH of C_5H_9), 2.5–3.4 (m, 2, CH_2 of C_5H_9), 3.8–4.4 (unsym. m, br, 12, $POCH_2$), 4.69 (q, 5, C_5H_5, ^3J(PCoCH) = 0.5 Hz).

[(Cyclopentadienyl)tris(diethylphosphito-*P*)cobalt-*O*,*O′*,*O″*]tricarbonyliodotungsten (5b). To a stirred solution of 546 mg (0.68 mmol) of **2b** in 170 mL of hexane was added dropwise a solution of 170 mg (0.67 mmol) of iodine in 60 mL of hexane. After 1 h, the solvent was decanted from the red–brown precipitate and the residue dried in vacuo. The solid was purified by chromatography through a column of alumina. Dichloromethane eluted a red band which was collected. Crystallization from dichloromethane/hexane at −20 °C afforded after 5 days 169 mg (0.18 mmol, 27%) of red crystals. The compound was air-stable in the solid state. It was also prepared from **2b** and triiodomethane: IR (KBr) ν(CO) 2003 (s), 1905 (vs), 1880 (s) cm^{-1}; ^{1}H NMR (80 MHz, CD_2Cl_2) δ 1.2 (t, 18, $POCH_2C\mathit{H}_3$), 4.1 (sym. m, 13 lines, 12, $POCH_2$), 5.0 (s, 5, C_5H_5); MS (160 °C), *m/e* (relative intensity) 930 (M^+, 1%), 902 (M^+ − CO, 30%), 874 (M^+ − 2CO, 23%). Anal. Calcd for $C_{20}H_{35}CoIO_{12}P_3W$: C, 25.83; H, 3.79. Found: C, 25.56; H, 3.66.

The homologous bromo complex **6b** has been prepared from **2b** and excess tribromomethane without solvent; reaction time ca. 12 h; IR ($CHBr_3$) ν(CO) 2018 (s), 1912 (s), 1888 (s) cm^{-1}.

The chloro complex **7b** was prepared from **2b** with tetrachloromethane; reaction time ca. 5 h; IR (KBr) ν(CO) 2017 (s), 1900 (s), 1876 (s) cm^{-1}.

Bis[(cyclopentadienyl)tris(diethylphosphito-*P*)cobalt-*O*,*O′*,*O″*]pentaoxoditungsten (8b). The crystalline hydrido complex **2b** (1.82 g, 2.26 mmol) was kept in air for 5 days to give a light-yellow powder. Some unreacted starting material was removed with hexane and the solid residue dried in vacuo. The product was taken up in acetone and the solution filtered from decomposition products and dried again in vacuo. The solid was then washed with ether, dissolved in dichloromethane, and crystallized from dichloromethane/pentane at −20 °C. After 2 weeks, large, yellow, clear crystals had formed which crumbled to a fine powder when dried at room temperature: yield 1.35 g (0.89 mmol, 79%); ^{1}H NMR (80 MHz, CD_3COCD_3) δ 1.25 (t, 36, $POCH_2C\mathit{H}_3$), 3.9–4.6 (unsym. m, 24, $POCH_2$), 5.11 (q, 5, C_5H_5, ^3J(PCoCH) = 0.4 Hz); IR (KBr) 902 (s, ν(W=O)), 802 (vs, br, ν(W—O—W)), 1130 (s, ν(P=O)), 590 (m, δ(P=O)) cm^{-1} in addition to the characteristic IR pattern of the tripod ligand L^-.[22] Anal. Calcd for $C_{34}H_{70}Co_2O_{23}P_6W_2$: C, 26.90; H, 4.65. M_r 1518. Found: C, 26.55; H, 4.63. M_r (osm. in CH_2Cl_2) 1540.

Bis[(cyclopentadienyl)tris(diethylphosphito-*P*)cobalt-*O*,*O′*,*O″*]titanium(1+) Hexafluorophosphate (9). To a solution of 530 mg (0.92 mmol) of $NaL \cdot H_2O$ in 20 mL of water was added a solution of ca. 0.4 mmol of Ti_{aq}^{3+} in aqueous hydrochloric acid. A blue–grey precipitate formed which was filtered off and immediately redissolved in methanol. The blue–violet product was precipitated with NH_4PF_6, filtered, washed with a little methanol, and dried in vacuo: yield 495 mg (0.39 mmol, 85%). Anal. Calcd for $C_{34}H_{70}Co_2F_6O_{18}P_7Ti$: C, 32.32; H, 5.58; Ti, 3.79. Found: C, 32.05; H, 5.57; Ti, 3.88.

Bis[(cyclopentadienyl)tris(diethylphosphito-*P*)cobalt-*O*,*O′*,*O″*]vanadium(1+) Hexafluorophosphate (10). To a saturated solution of 558 mg (0.97 mmol) of $NaL \cdot H_2O$ in water was added a freshly prepared solution of 80 mg (0.51 mmol) of VCl_3 and 250 mg (1.5 mmol) of NH_4PF_6 in 5 mL of water. A yellow precipitate formed which was separated by centrifugation, washed with water, and dried in vacuo. Recrystallization from acetone/ether yielded 330 mg (0.26 mmol, 54%) of **10** as greenish yellow crystals. Anal. Calcd for $C_{34}H_{70}Co_2F_6O_{18}P_7V$: C, 32.24; H, 5.57. Found: C, 32.06; H, 5.58.

Bis[(cyclopentadienyl)tris(diethylphosphito-*P*)cobalt-*O*,*O′*,*O″*]chromium(1+) Hexafluorophosphate (11). To a suspension of 166 mg (0.44 mmol) of $CrCl_3 \cdot 3THF$ in 10 mL of dry tetrahydrofuran was added a solution of 507 mg (0.91 mmol) of anhydrous NaL in 5 mL of tetrahydrofuran. The red–brown reaction mixture gradually became green after stirring for 24 h. The solvent was removed at reduced pressure, and the residue was extracted with 20 mL of water. Filtration through a membrane afforded a light-green solution from which the product **11** was precipitated by adding an excess of NH_4PF_6. The solid was separated by centrifugation, washed with water, and finally dissolved in dichloromethane. The organic phase was separated and pumped to dryness at reduced pressure. Crystallization from acetone/ether gave 270 mg (0.21 mmol, 48%) of light-yellow crystals. Anal. Calcd for $C_{34}H_{70}Co_2CrF_6O_{18}P_7$: C, 32.22; H, 5.57. Found: C, 31.86; H, 5.65.

Bis[(cyclopentadienyl)tris(diethylphosphito-*P*)cobalt-*O*,*O′*,*O″*]titanium(2+) Hexafluorophosphate (12). A solution of 480 mg (0.38 mmol) of **9** and 200 mg (1.23 mmol) of NH_4PF_6 in 20 mL of acetone was kept in air for 48 h after which time the color had changed to yellow. The solvent was removed at reduced pressure, and the residue was extracted

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(18) Brauer, G. *Handbuch der Präparativen Anorganischen Chemie*; F. Enke: Stuttgart, 1981; pp 1409–1411.

(19) Reference 18, p 1486.

(20) Allen, E. A.; Brisdon, B. J.; Fowles, G. W. A. *J. Chem. Soc.* **1964**, 4531.

(21) The ^{1}H and ^{13}C NMR data are not conclusive as to which of the possible isomers of the dimethylallyl groups is present in **4a** and **4b**.

(22) The IR spectra of all compounds containing the ligand L^- show the same typical pattern[3] with only the ν(P=O) and δ(P=O) bands being sensitive to the metal center coordinated to L^-.

with 15 mL of dichloromethane. Crystallization from dichloromethane/ether at −20 °C afforded 405 mg (0.29 mmol, 76%) of light-yellow fine crystals: ^{1}H NMR (80 MHz, CD_3NO_2) δ 1.38 (t, 36, $\mathrm{POCH_2C}H_3$), 4.28 (sym. m, 13 lines, 24, $POCH_2$), 5.49 (s, 10, C_5H_5). Anal. Calcd for $C_{34}H_{70}Co_2F_{12}O_{18}P_8Ti$: C, 28.99; H, 5.01. Found: C, 28.90; H, 5.24.

Bis[(cyclopentadienyl)tris(diethylphosphito-*P*)cobalt-*O*,*O*′,*O*″]oxovanadium (13). To a solution of 0.92 g (1.60 mmol) of NaL·H_2O in 10 mL of water was added $VOSO_4{\cdot}5H_2O$ in small portions until no more precipitation occurred. The product was separated by centrifugation, washed with water, and dried in vacuo. Repeated crystallization from pentane yielded 0.50 g (0.44 mmol, 55%) of greenish yellow crystals: IR (CCl_4) ν(V=O) 965 cm^{-1}. Anal. Calcd for $C_{34}H_{70}Co_2O_{19}P_6V$: C, 35.90; H, 6.20; Co, 10.36; P, 16.34; V, 4.48. Found: C, 36.05; H, 6.11; Co, 10.40; P, 16.16; V, 4.30.

[(Cyclopentadienyl)tris(diethylphosphito-*P*)cobalt-*O*,*O*′,*O*″]trichlorotin (14). To a freshly prepared solution of 254 mg (0.44 mmol) of NaL·H_2O in 5 mL of 2 M hydrochloric acid was added dropwise a solution of 267 mg (0.73 mmol) of $(NH_4)_2SnCl_6$ in 5 mL of 2 M hydrochloric acid. A yellow precipitate formed which was extracted into 10 mL of dichloromethane. The organic phase was separated and pumped to dryness at reduced pressure. Crystallization from dichloromethane/ether afforded 175 mg (0.23 mmol, 52%) of light-yellow crystals: ^{1}H NMR (270 MHz, CD_2Cl_2) δ 1.31 (t, 18, $\mathrm{POCH_2C}H_3$), 4.19 (sym. m, 13 lines, 12, $POCH_2$), 5.20 (s, 5, C_5H_5); MS (200 °C), *m/e* (relative intensity) 760 (M^+, 68%), 725 ($M^+ -$ Cl, 96%). Anal. Calcd for $C_{17}H_{35}Cl_3CoO_9P_3Sn$: C, 26.85; H, 4.64. Found: C, 26.68; H, 4.47.

[(Cyclopentadienyl)tris(diethylphosphito-*P*)cobalt-*O*,*O*′,*O*″]trichlorozirconium (15). A suspension of 120 mg (0.51 mmol) of $ZrCl_4$ and 285 mg (0.51 mmol) of NaL in 20 mL of dry tetrahydrofuran was stirred at room temperature for 48 h. The residue after evaporaion of the solvent was extracted three times with 10 mL of hexane to remove any unreacted NaL. The product was taken up in chloroform and crystallized from hexane/chloroform: yield 242 mg (0.33 mmol, 65%) of large-yellow crystals; ^{1}H NMR (80 MHz, $CDCl_3$) δ 1.32 (t, 18, $\mathrm{POCH_2C}H_3$), 4.21 (sym. m, 13 lines, 12, $POCH_2$), 5.20 (s, 5, C_5H_5); MS (165 °C), *m/e* (relative intensity) 732 (M^+, 56%), 697 ($M^+ -$ Cl, 88%). Anal. Calcd for $C_{17}H_{35}Cl_3CoO_9P_3Zr$: C, 27.86; H, 4.82. Found: C, 27.68; H, 5.11.

Tetraphenylphosphonium [(Cyclopentadienyl)tris(diethylphosphito-*P*)cobalt-*O*,*O*′,*O*″]trichlororhodate(1−) (16). To a stirred solution of 407 mg (0.71 mmol) of NaL·H_2O in 20 mL of tetrahydrofuran was added 200 mg (0.73 mmol) of $RhCl_3{\cdot}xH_2O$ (37.8% Rh). After 24 h the precipitate was filtered off, washed with a little tetrahydrofuran, and dried in vacuo to give a light-red powder. The filtrate contains the dimeric complex **17** and another not yet identified oxygen tripod ligand–rhodium complex. The dry powder was dissolved in 20 mL of water and precipitated with a saturated aqueous solution of PPh_4Cl. The precipitate was separated by centrifugation, washed with water, and dried in vacuo. Recrystallization from acetone/ether afforded 332 mg (0.31 mmol, 43%) of red shiny plates: ^{1}H NMR (80 MHz, CD_2Cl_2) δ 1.23 (t, 18, $\mathrm{POCH_2C}H_3$), 4.10 (sym. m, 13 lines, 12, $POCH_2$), 5.00 (s, 5, C_5H_5). Anal. Calcd for $C_{41}H_{55}Cl_3CoO_9P_4Rh$: C, 45.43; H, 5.11. Found: C, 45.53; H, 5.10.

Di-μ-chlorobis{[(cyclopentadienyl)tris(diethylphosphito-*P*)cobalt-*O*,*O*′,*O*″]chlororhodium} (17). A mixture of 400 mg (0.69 mmol) of NaL·H_2O and 200 mg (0.73 mmol) of $RhCl_3{\cdot}xH_2O$ (37.8% Rh) in 20 mL of methanol was heated to reflux for 18 h. The resulting dark-red solution was separated from black solid decomposition products and concentrated to ca. 10 mL. Addition of 20 mL of ether precipitated NaCl and presumably some Na[$LRhCl_3$]. The supernatant solution was concentrated to yield a red oil which was dried in high vacuum. A chloroform solution of the oil was covered with hexane and kept at −20 °C. After a few days, dark-red crystals had grown which were separated and dried in vacuo: ^{1}H NMR (80 MHz, CD_2Cl_2) δ 1.24, 1.28, 1.31 (3 overlapping t, 36, $\mathrm{POCH_2C}H_3$, ^3J(HCCH) = 7 Hz), 3.9–4.4 (unsym. m, br, 24, $POCH_2$), 5.06 (q, 10, C_5H_5, ^3J(PCoCH) = 0.4 Hz). Anal. Calcd for $C_{34}H_{70}Cl_4Co_2O_{18}P_6Rh_2$: C, 28.79; H, 4.97; Cl, 10.00; Rh, 14.51. Found: C, 28.65; H, 5.10; Cl, 9.88; Rh, 14.35.

[(Cyclopentadienyl)tris(diethylphosphito-*P*)cobalt-*O*,*O*′,*O*″]dichlorooxomolybdenum (18). A suspension of 224 mg (0.70 mmol) of [$MoCl_4(CH_3CN)_2$] and 400 mg (0.72 mmol) of dry NaL in 15 mL of tetrahydrofuran was stirred for 24 h at room temperature. The dark-red solution was separated from insoluble NaCl and concentrated at reduced pressure to yield a red–brown sticky residue. This was extracted with hexane to give immediately a blue hexane solution and a small amount of a viscous red–brown oil. Long green needles crystallized from the hexane solution at −78 °C, which were collected: yield 260 mg (0.36 mmol, 52%); MS (150 °C), *m/e* (relative intensity) 719 (M^+, 63%), 684 ($M^+ -$ Cl, 5%), 649 ($M^+ -$ 2Cl, 3%). Anal. Calcd for $C_{17}H_{35}Cl_2CoMoO_{10}P_3$: C, 28.43; H, 4.91; Cl, 9.87; Mo, 13.36. Found: C, 28.16; H, 5.25; Cl, 9.79; Mo, 13.27.

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Supplementary Material Available: Tables II–IV listing anisotropic thermal parameters, bond lengths, and bond angles (8 pages); tables of calculated and observed structure factors (45 pages). Ordering information is given on any current masthead page.

Thermodynamic Studies of Donor Binding to Heterogeneous Catalysts

Yau Yan Lim, Russell S. Drago,* Michael W. Babich, Ngai Wong, and Peter E. Doan

Contribution from the University of Florida, Gainesville, Florida 32611, and the Florida Institute of Technology, Melbourne, Florida 32901. *Received November 14, 1985*

Abstract: The thermodynamic data for the adsorption of pyridine, *N*-methylimidazole, and dimethylcyanamide from cyclohexane onto palladium oxide crystallites supported on carbon (5% w/w) were obtained by calorimetric and adsorption studies. The data indicated that there are at least two acceptor sites on the palladium oxide surface. Both the calorimetric and adsorption experiments give the same saturation adsorption capacity for site 1. Its magnitude suggests that the adsorbed pyridine is normal to the surface plane of palladium oxide, indicating that the adsorption process involves a Lewis acid–base type of interaction. In the low-coverage region, the adsorption quotients of base onto palladium oxide are considerably larger than those of carbon, indicating a preferential adsorption of base onto the palladium oxide surface.

Reactions of gases and liquids at solid interfaces are an important, fundamental process in heterogeneous catalysis.[1] Relatively little information is available concerning the binding of any but the simplest gas molecules to a solid interface. Consequently, little is known about the electronic nature of the gas–solid or liquid–solid interaction. Uncertainty often exists about the geometry of the adsorbate relative to the metal surface and whether or not to describe the interaction as Lewis acid–base in nature.[2] The relationship of the metal–ligand bond strength to

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