Nitrogen Tripod Ligand/Oxygen Tripod Ligand Indium(III) Complexes: The First Structurally Characterized Trofimenko−Kläui Complex $[\eta^5\text{-}(C_5H_5)Co\{P(OCH_3)_2(O)\}_3InHB(pz)_3][InCl_4]$ (pz = pyrazol-1-yl)

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Keywords: Hard and soft acids and bases concept (HSAB) / Symbiosis and antisymbiosis / Indium / (Cyclopentadienyl)tris(diorganylphosphito-*P*)cobaltate(1−) / Hydrotris(pyrazol-1-yl)borate / Mixed-ligand complexes

Indium(III) complexes $[L_RInTp^*]X$ {L_R = (cyclopentadienyl)-tris[diorganylphosphi(ni)to-*P*]cobaltate(1−) $[\eta^5\text{-}(C_5H_5)Co\{PR_2(O)\}_3]^-$, R = OCH_3, CH_2CH_3; Tp* = hydrotris(3,5-dimethylpyrazol-1-yl)borate} have been prepared from $[Tp^*InCl_2(NCCH_3)]$ and AgL_{OMe} or TlL_{Et}. Alternatively, equilibration of a 1:1 mixture of the homoleptic complexes $[In(L_{OMe})_2][PF_6]$ and $[In(Tp)_2][PF_6]$ in aqueous methanol slowly yielded the heteroleptic indium(III) complex $[L_{OMe}InTp][PF_6]$. An X-ray crystal structure determination revealed a *fac*-N_3O_3 coordination sphere for the $[L_{OMe}InTp][InCl_4]$ complex. These indium compounds represent the first structurally characterized complexes where the tripodal oxygen ligand L_R and the tripodal nitrogen ligand Tp are coordinated to the same metal center. Indium(III) is classified as a class a, i.e. a hard metal ion, but it evidently prefers an antisymbiotic arrangement of ligands.

Introduction

Jørgensen defined chemical symbiosis as the fact that hard bases (electronegative donor atoms) attached to a given central atom make it a harder Lewis acid by retaining their valence electrons thus maintaining a high positive charge on the central atom.[1] Soft bases (donor atoms of low electronegativity) attached to the same central atom give up their valence electrons thereby reducing its positive charge and making it a softer Lewis acid. Pearson, on the other hand, pointed out that class b metal ions very often behave in an antisymbiotic manner. Thus, soft bases attached to an already soft Lewis acid decrease its affinity towards another soft base.[2] Antisymbiosis can be explained on the basis of the *trans* effect or *trans* influence and is most pronounced in square planar $4d^8$ and $5d^8$ complexes. Symbiosis seems to be the preferred behaviour of class a, i.e. hard metal ions.

The tridentate oxygen and nitrogen ligands **1** and **2** (see Figure 1), that we introduced some time ago,[3,4] are both facially coordinating monoanionic six-electron ligands. The tripodal nitrogen ligands, abbreviated herein as Tp, exhibit coordination chemistry resembling that of cyclopentadienyl or pentamethylcyclopentadienyl ligands. On the other hand, tripodal oxygen ligands, abbreviated herein as L_R, are very hard and weak ligands. Indeed, they are weaker than water and nearly as hard as fluoride. Both form 2:1 complexes with a wide variety of main group and transition metal ions M^{2+} and M^{3+}. All our attempts to synthesize hard-soft mixed-ligand 2:1 complexes starting from metal salts MX_2 and alkali metal salts of **1** and **2** have been unsuccessful. We obtained only mixtures of the homoleptic complexes and the question that arises is whether this was a consequence of strict symbiosis? In the following, we describe the synthesis and characterization of octahedral mixed-ligand indium(III) complexes, i.e. indium(III) complexes with an InN_3O_3 coordination polyhedron.

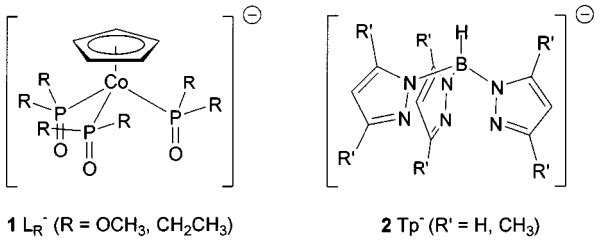

Figure 1. Structures of Kläui's and Trofimenko's ligands **1** and **2**

Results and Discussion

Preparative Results

Reactions of the silver and thallium salts of the oxygen ligands, e.g. AgL_{OMe} (**1a**) and TlL_{Et} (**1b**), with the indium complex $[Tp^*InCl_2(NCCH_3)]$ (**6**)[5] lead to compounds $[L_{OMe}InTp^*][AgCl_2]$ (**3d**) and $[L_{Et}InTp^*]Cl$ (**3c**) (see Figure 2).

The reactions of the silver and thallium salts are fast and go to completion. The corresponding alkali metal salts re-

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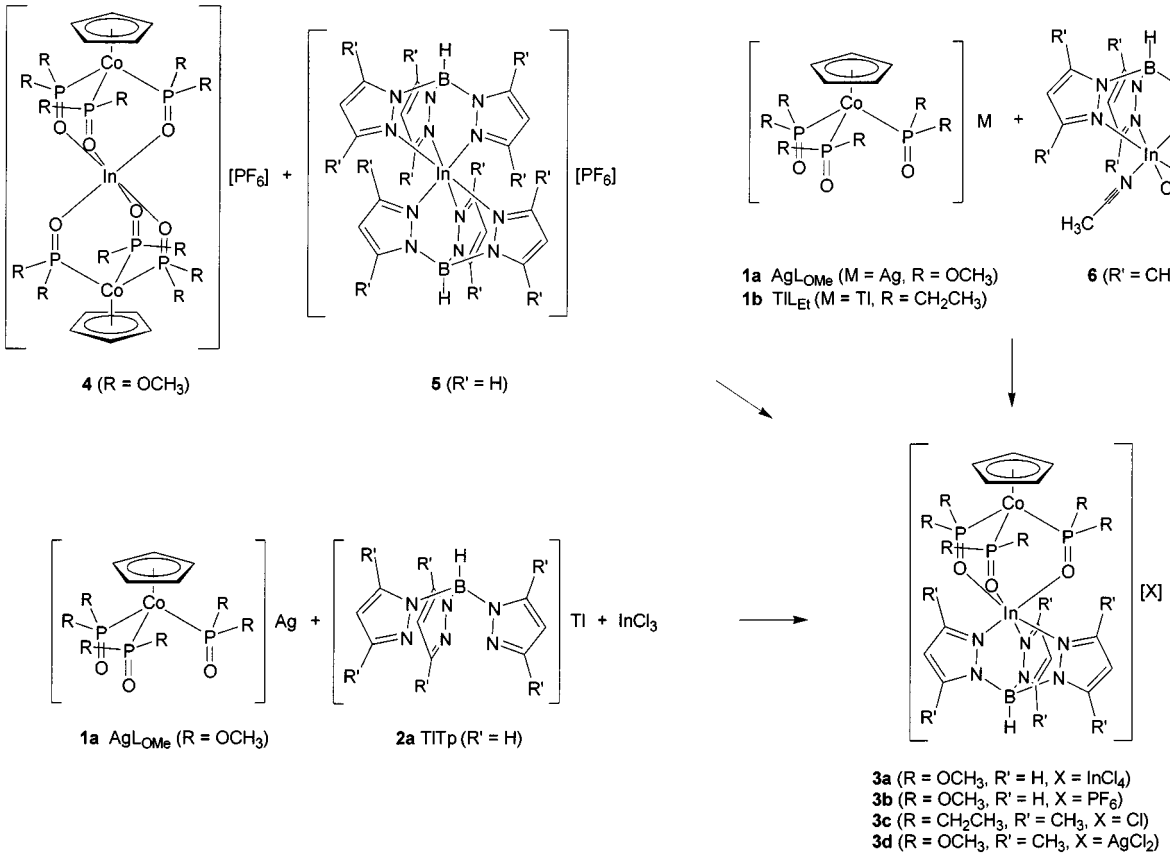


Figure 2. Synthesis and schematic structures of the indium(III) complexes

act more sluggishly and the need to separate the remaining starting compounds makes purification of the complexes **3** more difficult.

We had no evidence as to whether the successful preparation of the heteroleptic indium complexes $[L_{OMe}InTp^*]^+$ and $[L_{Et}InTp^*]^+$ was kinetically or thermodynamically controlled. Therefore, we performed a second experiment in which indium chloride was treated with AgL_{OMe} (**1a**) and TlTp (**2a**) in a mixture of dichloromethane, acetone, and methanol. $[L_{OMe}InTp][InCl_4]$ (**3a**) was isolated in almost quantitative yield. We could not detect any of the homoleptic complexes $[In(L_{OMe})_2]^+$ or $[In(Tp)_2]^+$. Finally, we tried to equilibrate an equimolar mixture of the homoleptic compounds $[In(L_{OMe})_2][PF_6]$ (**4**) and $[In(Tp)_2][PF_6]$ (**5**) in methanol/water. At room temperature, we found there to be very little or no ligand exchange. After refluxing the solution for 2 d, we were able to recover the heteroleptic compound $[L_{OMe}InTp][PF_6]$ (**3b**) together with some of the unchanged homoleptic complexes **4** and **5**. However, the solubilities of **3b**, **4**, and **5** are rather similar and we have not been able to separate the compounds. Identification of **3b**, **4**, and **5** was nevertheless possible on the basis of their ^1H and ^{31}P NMR spectra. Complete equilibration could not be attained by prolonged heating. The Tp ligand is slowly hydrolyzed under these conditions.

Complexes **3** were obtained as bright-yellow crystals, and were found to be stable in moist air and soluble in acetone, nitromethane, and dichloromethane, moderately soluble in chloroform, diethyl ether, and methanol/water mixtures, and insoluble in hydrocarbons.

MS Data, IR Spectra, and Conductivity Measurements

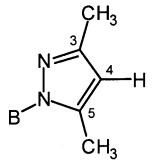
The mass spectra of complexes **3** were measured by the fast atom bombardment (FAB^+) ionization technique using a nitrobenzyl alcohol matrix. The molecular ion peaks $[L_RInTp]^+$ and $[L_RInTp^*]^+$ were the base peaks of the spectra and could easily be recognized from the characteristic isotope pattern. The only other strong peaks were those corresponding to the fragment $[L_RIn + H]^+$, generated by loss of the Tp or Tp* ligand from the molecular ion.

The IR spectra of complexes **3a**−**3d** were found to be dominated by the characteristic absorptions of the ligands **1**[6] and **2**.[4] Conductivity measurements[7] of 10^{-3} M solutions of **3a** and **3d** in nitromethane indicated that these compounds behave as 1:1 electrolytes in solution.

1D and 2D NMR Spectra

The ^1H NMR spectra of **3a**−**3d** feature only a few peaks that can easily be assigned to either ligand **1** or ligand **2**. In complexes **3a** and **3b**, the pyrazol-1-yl protons give rise to an AMX spin system and the ^1H NMR spectra reveal local C_{3v} symmetry of the ligands. In the ^1H NMR spectra of **3c** and **3d**, the protons of the methyl groups in the 3- and 5-positions of the pyrazol-1-yl rings appear as singlets, as do the 4-H protons (ratio 3:3:1), again indicating local C_{3v}

Table 1. Chemical shifts (δ) of the free ligands and of the heteroleptic complexes **3c** and **3d**; pz = pyrazol-1-yl, L_R^- = (cyclopentadienyl)tris-[diorganylphosphi(ni)to-*P*]cobaltate(1−)



Compound	^{1}H NMR							^{31}P{1H} NMR
	3-CH_3-pz (Tp^{*-})	4-H-pz (Tp^{*-})	5-CH_3-pz (Tp^{*-})	C_5H_5 (L_R^-)	OCH_3 (L_{OMe}^-)	CH_2CH_3 (L_{Et}^-)	CH_2CH_3 (L_{Et}^-)	P (L_R^-)
NaL_{OMe} [a]	–	–	–	5.06	3.61			110.0
TlL_{Et} (**1b**)[a]	–	–	–	4.88	–	1.22	2.10 2.30	108.5
KTp*[b]	2.05[c]	5.58	2.21[c]	–	–	–	–	–
$[L_{OMe}InTp^*][AgCl_2]$ (**3d**)[a]	2.46	5.88	2.40	5.46	3.84	–	–	117.8
$[L_{Et}InTp^*]Cl$ (**3c**)[a]	2.36	5.81	2.35	5.47	–	1.31	2.5	119.7

[a] [D_1]Chloroform. – [b] [D_6]Acetone. – [c] The 3- and 5-positions of the pyrazol-1-yl rings were not distinguished.

symmetry of the ligands. The two upfield resonances due to the methyl groups cannot be unequivocally assigned to the 3- and 5-positions solely on the basis of the 1D ^{1}H NMR spectrum.[8]

In the ^{31}P{^{1}H} NMR spectra, the phosphito and phosphinito groups of the tripodal oxygen ligand give rise to a singlet resonance at δ ≈ 110, which is broadened by quadrupolar relaxation (^{59}Co, I = 7/2). Coordination of the ligand to indium(III) decreases the electronic shielding and δ^{31}P is consequently shifted to lower field by about 10 ppm to δ ≈ 120 (see Table 1).

The ^{1}H NMR spectrum of ligand **1a** features a four-line pattern ("*virtual* quadruplet") due to the methoxy groups of L_{OMe}^- (OCH_3, $[A[X_3]_2]_3$ spin system, $^3J_{H\text{-}P}$ = 11.1 Hz). These resonances are shifted to lower field in **3d** as compared to those in **1** (see Table 1). The ^{1}H NMR spectrum of the ligand L_{Et}^- (**1b**) features unresolved multiplet patterns due to the methyl groups (CH_2CH_3, $[A[X_3YZ]_2]_3$ spin system) and the methylene groups (CH_2CH_3, $[A[X_3YZ]_2]_3$ spin system), which are shifted to lower field in **3c**. Coordination to indium(III) also shifts the signals due to the pyrazol-1-yl ring protons and methyl groups to lower field (see Table 1).

All the NMR-spectroscopic data of compounds **3** are in agreement with their formulation as mixed-ligand complexes $[L_RInTp]^+$ and $[L_RInTp^*]^+$ in solution. However, the chemical shift differences between the mixed-ligand complexes and the homoleptic complexes are rather small and are not always sufficient to discern e.g. $[L_{Et}InTp^*]^+$ from an equimolar mixture of $[In(L_{Et})_2]^+$ and $[In(Tp^*)_2]^+$. We have recently found[9] that the coordination of an oxygen ligand and a nitrogen ligand to the same indium ion can be proven by 2D ^{1}H NOESY NMR spectroscopy. In this way, one can identify $[L_RInTp]^+$ and $[L_RInTp^*]^+$ and exclude fast ligand exchange between homoleptic and heteroleptic complexes.[9]

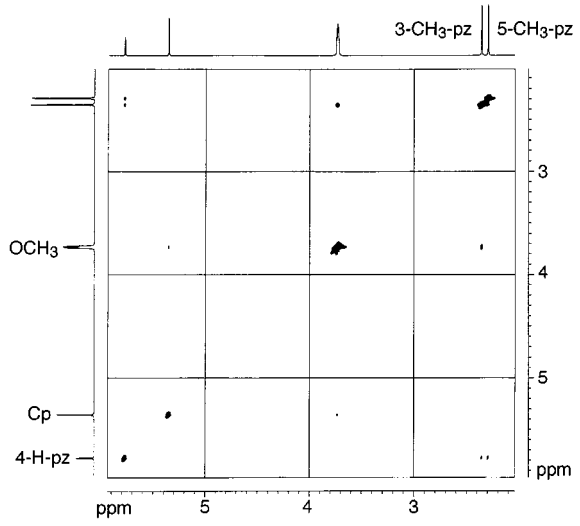


Figure 3. 2D ^{1}H NOESY NMR spectrum of **3d** ([D_6]acetone); a strong cross-peak is observed between the methoxy groups of the oxygen ligand and *only one* (!) of the pyrazol-1-yl ring methyl groups of the nitrogen ligand

Table 2. 2D ^{1}H NOESY NMR correlations in the heteroleptic complex $[L_{OMe}InTp^*][AgCl_2]$ (**3d**); pz = pyrazol-1-yl, L_{OMe}^- = (cyclopentadienyl)tris(dimethylphosphito-*P*)cobaltate(1−)

NOE correlation	
of H-	with H-
OCH_3 (L_{OMe}^-)	C_5H_5 (L_{OMe}^-), 3-CH_3-pz
C_5H_5 (L_{OMe}^-)	OCH_3 (L_{OMe}^-)
4-H-pz	3-CH_3-pz, 5-CH_3-pz
3-CH_3-pz	4-H-pz, OCH_3 (L_{OMe}^-)
5-CH_3-pz	4-H-pz

Such NOESY NMR spectra (see Figure 3, Table 2) show correlation signals between the cyclopentadienyl ligand and the methoxy groups of the oxygen ligand, as well as interac-

tions between the pyrazol-1-yl 4-H ring proton and the 3-CH_3-pz and 5-CH_3-pz methyl groups. Additionally, a strong cross-peak is observed between the methoxy groups of the oxygen ligand and only *one* of the pyrazol-1-yl ring methyl groups of the nitrogen ligand, a result that can only be obtained if both ligands are coordinated to the same metal ion, thus confirming the spatial proximity of the two ligands as depicted in Figure 2. This cross-peak also leaves no ambiguity concerning the assignment of 3-CH_3 and 5-CH_3 of the pyrazol-1-yl rings.

We expected the mixed-ligand complexes identified in solution to also exist in the solid state. A single-crystal X-ray analysis of complex **3a** confirmed this hypothesis (see Figure 4).

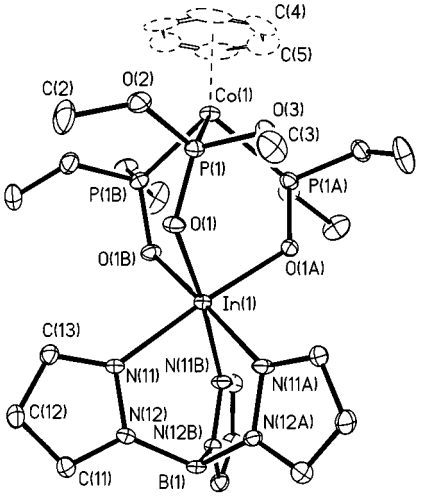


Figure 4. Thermal ellipsoid plot (at a 30% probability level) for the cation of **3a**; the disordered cyclopentadienyl ring is represented by the six atoms above Co(1); hydrogen atoms and the $[InCl_4]^-$ ion are omitted for the sake of clarity

Crystal Structure of $[L_{OMe}InTp][InCl_4]$ (3a)

A thermal ellipsoid plot of **3a** is shown in Figure 4; for crystal data see Table 3. Both ions in the lattice are positioned along a threefold axis. The Cp ring of the ligand is perpendicular to the crystallographic threefold axis. As a result, threefold disorder is imposed upon the five-membered ring. For the Cp system, two unique positions of the C atoms were found in the asymmetric unit. The occupancy for each position was set at 0.83325 so that C(4) and C(5) represent one-third of the cyclopentadienyl ring. The distance from Co(1) to the centroid of the calculated ring was found to be 1.69 Å. The hydrogen atoms on C(4) and C(5) were ignored.

Conclusions

The results of this study have shown that the hard class a metal ion indium(III) can behave in an antisymbiotic manner. The different steric properties of the Tp and Tp* ligands do not influence the course of the reaction.

As far as we are aware, there have been no detailed investigations of the preferences for symbiosis or antisymbiosis of hard metal ions. Hegetschweiler[10] has looked at the coordination chemistry of 1,3,5-triamino-1,3,5-trideoxy-*cis*-inositol (taci) towards the Group 13 metal ions Al^{3+}, Ga^{3+}, and Tl^{3+}. It was found that taci can act as a tridentate ligand in four different binding modes (O_3, O_2N, ON_2, and N_3). X-ray crystal structure determinations revealed AlO_6, GaN_3O_3, and TlN_6 coordination spheres for the respective $[M(taci)_2]^{3+}$ complexes. These results fit nicely with our finding of an InN_3O_3 coordination sphere for the $[L_RInTp]^+$ and $[L_RInTp^*]^+$ complexes.

Table 3. Crystal data and structure refinement for **3a**

Empirical formula	$C_{20}H_{33}BCl_4CoIn_2N_6O_9P_3$
Formula mass	1035.61
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system	cubic
Space group	$P2(1)3$
Unit cell dimensions	a = 15.6051(2) Å
b = 15.6051(2) Å	
c = 15.6051(2) Å	
Volume	3800.14(8) Å^3
Z	4
Density (calculated)	1.810 Mg/m^3
Absorption coefficient	2.092 mm^{-1}
F(000)	2040
Crystal size	0.30 × 0.25 × 0.20 mm
θ range for data collection	2.26 to 28.36°
Index ranges	$-20 \le h \le 18$
	$-19 \le k \le 20$
	$-20 \le l \le 20$
Reflections collected	17289
Independent reflections	3077 [R(int) = 0.0427]
Completeness to θ = 28.36°	97.7%
Absorption correction	empirical from SADABS
Max. and min. transmission	0.6797 and 0.5725
Refinement method	full-matrix least squares on F^2
Data/restraints/parameters	3077/0/142
Goodness-of-fit on F^2	1.681
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0309, wR_2 = 0.0601
R indices (all data)	R_1 = 0.0348, wR_2 = 0.0613
Absolute structure parameter	0.05(2)
Largest diff. peak and hole	0.328 and −0.519 e Å^{-3}

Although the synthesis of $[L_RMTp]$ (M = Pb, Sn; R = OCH_2CH_3) has been reported in the literature,[11] the complexes were not characterized by X-ray analysis. We tried to synthesize $[L_{OEt}PbTp]$ (**9**) according to the published procedure (Figure 5). At 328 K, the 1D ^{1}H NMR spectrum of the product displayed two sets of signals like those reported in the literature,[11] which could readily be assigned to the two ligands with local C_{3v} symmetry. At 223 K, a doubling of the number of signals was observed. These well-separated signals were indicative of the presence of three species, which we assign as the heteroleptic complex $[L_{OEt}PbTp]$ (**9**) and the homoleptic complexes $[(L_{OEt})_2Pb]$ (**10**) and $[Tp_2Pb]$ (**11**). This hypothesis was supported by the relevant intensity ratios. The existence of **9** was corroborated by a 2D ^{1}H NOESY NMR spectrum (223 K), which showed a cross-peak between the OCH_2CH_3 groups of the oxygen ligand and only one of the pyrazol-1-yl ring protons of the nitrogen ligand. A 2D ^{1}H EXSY NMR spectrum (223 K) featured interchange signals between the pyrazol-1-yl ring protons in the 3- and 5-positions as well as between both Cp signals of the oxygen ligand, thus revealing an equilibrium

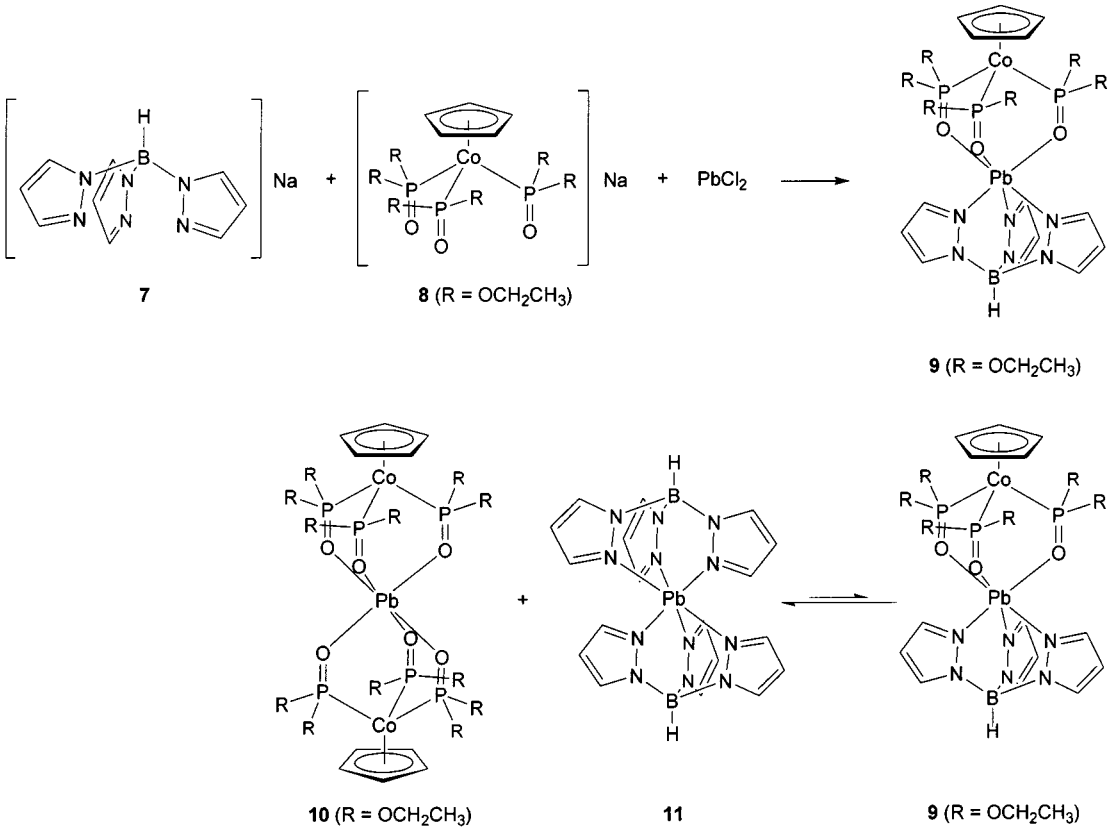


Figure 5. Equilibrium between the homoleptic and heteroleptic lead(II) complexes

Table 4. ^{207}Pb chemical shifts (δ) of the homoleptic and heteroleptic lead(II) complexes; Tp = tris(pyrazol-1-yl)borate, L_{OEt} = (cyclopentadienyl)tris(diethylphosphito-*P*)cobaltate; lead chemical shifts are highly dependent on temperature and concentration (0.05 M solution in $CDCl_3$)

Compound		^{207}Pb NMR ($\nu_{1/2}$/Hz)		
		Literature values	303 K	223 K
1:1 mixture of **10** and **11**		–	–	−2037, −1614 (120), −1309 (96)
"[TpPbL$_{OEt}$]"	(**9**)	−1613 (110)	–	−2032 (362), −1615 (193), −1311 (169)
[(L$_{OEt}$)$_2$Pb]	(**10**)	−2034 (320)	−2056 (55) sept., $^2J_{PbP}$ = 72 Hz	−2005 (335)
[(Tp)$_2$Pb]	(**11**)	−895 (600)	−1244 (72)	−1312 (99)

between **9**, **10**, and **11** in solution. At ambient temperatures, this equilibrium is fast on the proton NMR time scale.

The ^{31}P{^{1}H} NMR spectrum featured two well-separated signals at 223 K, which could be assigned to **9** and **10**. The ^{207}Pb NMR spectrum showed the resonances of the homoleptic complexes **10** and **11**, as well as a third signal that could most probably be assigned to **9** (see Table 4).

A solution of a mixture of the homoleptic complexes **10** and **11** in a 1:1 molar ratio exhibits exactly the same spectroscopic properties and gives an identical elemental analysis as reported for **9** in the literature. The very similar physical properties of these complexes as well as the fast equilibrium between **9**, **10**, and **11** in solution most probably account for the fact that neither Reger[11] nor ourselves have been able to isolate **9** as a pure compound.

It seems impossible to make general predictions as to whether a class a, i.e. a hard metal ion, will prefer a symbiotic or an antisymbiotic ligand arrangement. A more systematic investigation should give better insight into the relationship between HSAB properties and symbiotic and antisymbiotic behaviour.

Experimental Section

General Procedures: Standard inert-atmosphere techniques were used for syntheses and sample manipulations. The solvents were dried by standard methods, distilled under nitrogen, and stored over 4 Å molecular sieves prior to use. Acetone p.a. and nitromethane p.a. (E. Merck, Darmstadt) were used as obtained and stored over 4 Å molecular sieves. – ^{1}H, 2D ^{1}H NOESY, 2D ^{1}H EXSY,

$^{31}P\{^1H\}$, and ^{207}Pb NMR spectra were recorded with a Bruker Analytische Meßtechnik DRX 500 NMR spectrometer from 0.05 M solutions. The ^1H NMR spectra were calibrated against the residual proton signals of the solvents as internal references ([D_6]acetone: δ_H = 2.08; [D_1]chloroform: δ_H = 7.24), while the $^{31}P\{^1H\}$ NMR spectra were referenced to external 85% H_3PO_4. Chemical shifts are accurate to within ±0.01 ppm for δ^1H, ±0.1 ppm for $\delta^{31}P$, and ±1 ppm for $\delta^{207}Pb$. For acquisition of the ^{207}Pb NMR spectra, the following parameters were typically used: sweep width 10^5 Hz, 4 k data points, 90° pulse. ^{207}Pb chemical shifts are reported downfield from tetramethyllead using 1 M aq. $Pb(NO_3)_2$ ($\delta^{207}Pb$ = −2961) as an external standard. The phase-sensitive NOESY spectra[12] were obtained with 512 t_1 increments and 2048 data points in t_2; 16 free induction decays were collected for each value of t_1. After zero-filling and multiplying both dimensions with a q sine function, the data were Fourier-transformed into a 1024 × 1024 matrix. The mixing time used was 0.9 s. − Infrared spectra were recorded with a Bruker Analytische Meßtechnik IFS 66 FT-IR spectrometer. − FAB^+ mass spectra were recorded with a Finnigan MAT 8200 mass spectrometer. − Elemental analyses were provided by the Institut für Pharmazeutische Chemie at the Heinrich-Heine-Universität Düsseldorf and the Mikroanalytisches Labor Pascher, Remagen. − Conductivity measurements were performed using a Schott CG 851 conductometer. − The sodium salt of **1**[13] and compounds **1a**,[9] **1b**,[14] **3a**,[9] **3b**,[9] **4**,[9] **5**,[9] **6**,[5] **7**,[4] **8**,[15] **10**,[16] and **11**[4] were prepared according to published procedures. The thallium salt **2a** was prepared from KTp and Tl_2CO_3 according to procedures for analogous TlTp compounds.[17] All other compounds were purchased from commercial sources.

Crystal Structure Determination of 3a: Diffraction data were collected with a Siemens P4 diffractometer equipped with a CCD area detector. Crystal data are presented in Table 3. The cubic unit cell was determined using reflections collected from three series of 15 frames in distinct regions of space. Final unit-cell refinement was performed by a least-squares fitting of 6886 reflections. The systematic absences were consistent with the space groups $P2_13$ and $P4_232$; Laue group symmetry supported the former choice. The E statistics for the data, with a value of 0.687, also supported this choice. The structure was solved by direct methods and the remaining atoms were located by difference Fourier synthesis. The reported absolute stereochemistry was confirmed by refinement of the Flack parameter [0.05(2)]. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions and treated as isotropic contributions with thermal parameters defined as 1.2 or 1.5 times that of the parent atom. All software and sources of scattering factors are contained in the SHELXTL program library (version 5.10, G. Sheldrick, Bruker-AXS, Madison, WI).

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-151641. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Preparations

{(Cyclopentadienyl)tris(dimethylphosphito-*P*)cobalt-*O*,*O*′,*O*′′}-{hydrotris(3,5-dimethylpyrazol-1-yl)borato-*N*,*N*′,*N*′′}indium Dichloroargentate [L_{OMe}InTp*][$AgCl_2$] (3d): A colourless solution of **6** (0.44 g, 0.92 mmol) in dichloromethane (20 mL) was treated with **1a** (0.52 g, 0.92 mmol) and the resulting mixture was stirred at room temperature. After a few minutes, the solution turned cloudy and the precipitation of a white solid was observed. The reaction mixture was stirred overnight, then filtered through Celite, and the filtrate was concentrated in vacuo. The resulting yellow residue was redissolved in the minimum volume of dichloromethane and this solution was treated with an excess of *n*-hexane. A pale-yellow oily residue precipitated immediately, which solidified on ultrasound treatment. The yellow solid was repeatedly washed with small amounts of *n*-hexane and dried in vacuo. Slow diffusion of diethyl ether into a dichloromethane solution yielded yellow crystals. Yield: 0.86 g (94%). − ^1H NMR (298 K, [D_1]chloroform): δ = 2.40 (s, 9 H, 5-CH_3-pz), 2.46 (s, 9 H, 3-CH_3-pz), 3.84 (virt. q, [A[X_3]$_2$]$_3$ $^3J_{H-P}$ = 11.1 Hz, 18 H, OCH_3 L_{OMe}), 5.46 (s, 5 H, C_5H_5 L_{OMe}), 5.88 (s, 3 H, 4-H-pz). − $^{31}P\{^1H\}$ NMR (298 K, [D_1]chloroform): δ = 117.8 {s, [*A*[X_3]$_2$]$_3$, *P*(O)OCH_3}. − IR (KBr): $\tilde{\nu}$ = 2559 cm^{-1} (m) ν(B−H), 1103 (vs), 1071 (vs) ν(P=O), 647 (m), 587 (s) δ(P=O). − $C_{26}H_{45}AgBCl_2CoInN_6O_9P_3$ (1041.94): calcd. C 29.97, H 4.35, N 8.07, Ag 10.35, In 11.02; found C 30.07, H 4.36, N 8.05, Ag 10.2, In 11.0. − FAB^+ MS; *m*/*z* (%): 863 [M − Cl]$^+$ (100), 567 [L_{OMe}In + H]$^+$ (43). − Conductivity (10^{-3} M solution of **3d** in nitromethane): Λ = 73 μS.

{(Cyclopentadienyl)tris(diethylphosphinito-*P*)cobalt-*O*,*O*′,*O*′′}-{hydrotris(3,5-dimethylpyrazol-1-yl)borato-*N*,*N*′,*N*′′}indium Chloride [L_{Et}InTp*]Cl (3c): According to the procedure described above for **3d**, complex **3c** was obtained as a yellow powder from **6** (0.70 g, 1.46 mmol) and **1b** (0.94 g, 1.46 mmol). Yield: 1.26 g (97%). − ^1H NMR (298 K, [D_1]chloroform): δ = 1.31 {m, [A[X_3YZ]$_2$]$_3$, 18 H, P(O)CH_2CH_3 L_{Et}}, 2.35 (s, 9 H, 5-CH_3-pz), 2.36 (s, 9 H, 3-CH_3-pz), 2.5 {m, [A[X_3YZ]$_2$]$_3$, 12 H, P(O)CH_2CH_3 L_{Et}}, 5.47 (d, 5 H, $^3J_{H-P}$ = 0.4 Hz, C_5H_5 L_{Et}), 5.81 (s, 3 H, 4-H-pz). − $^{31}P\{^1H\}$ NMR (298 K, [D_1]chloroform): δ = 119.7 {s, [*A*[X_3YZ]$_2$]$_3$, *P*(O)OCH_3}. − IR (KBr): $\tilde{\nu}$ = 2555 cm^{-1} (m) ν(B−H), 1070 (vs) ν(P=O), 648 (m), 538 (vs) δ(P=O). − $C_{32}H_{57}BClCoInN_6O_3P_3$ (886.01): calcd. C 43.34, H 6.48, N 9.48; found C 41.85, H 6.55, N 9.11. − FAB^+ MS; *m*/*z* (%): 851 [M − Cl]$^+$ (100), 555 [L_{Et}In + H]$^+$ (48).

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[1] C. K. Jørgensen, *Inorg. Chem.* **1964**, *3*, 1201.
[2] R. G. Pearson, *Inorg. Chem.* **1973**, *12*, 712.
[3] W. Kläui, *Angew. Chem.* **1990**, *102*, 661; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 627.
[4] S. Trofimenko, *Scorpionates: The Coordination Chemistry of Polypyrazolylborate Ligands*, Imperial College London, **1999**, and references therein.
[5] A. H. Cowley, C. J. Carrano, R. L. Geertz, R. A. Jones, C. M. Nunn, *Angew. Chem.* **1988**, *100*, 306; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 277.
[6] W. Kläui, K. Dehnicke, *Chem. Ber.* **1978**, *111*, 451.
[7] W. J. Geary, *Coord. Chem. Rev.* **1971**, *7*, 81.
[8] C. Lopez, R. M. Claramunt, D. Sanz, C. Foces Foces, F. H. Cano, R. Faure, E. Cayon, J. Elguero, *Inorg. Chim. Acta* **1990**, *176*, 195.
[9] W. Kläui, N. Liedtke, W. Peters, *Magn. Res. Chem.* **1999**, *37*, 867.
[10] K. Hegetschweiler, M. Ghisetta, T. F. Fässler, R. Nesper, H. W. Schmalle, G. Rihs, *Inorg. Chem.* **1993**, *32*, 2032.
[11] D. L. Reger, Y. Ding, A. L. Rheingold, R. L. Ostrander, *Inorg. Chem.* **1994**, *33*, 4226.
[12] J. Jeener, P. Bachmann, R. R. Ernst, *J. Chem. Phys.* **1979**, *71*, 4546.
[13] W. Kläui, B. Lenders, B. Hessner, K. Evertz, *Organometallics* **1988**, *7*, 1357.

[14] W. Kläui, A. Kremer-Aach, N. Liedtke, unpublished results.
[15] W. Kläui, *Z. Naturforsch., B* **1979**, *34*, 1403.
[16] E. M. Holt, W. Kläui, J. J. Zuckerman, *J. Organomet. Chem.* **1987**, *335*, 29.
[17] S. Trofimenko, J. C. Calabrese, P. J. Domaille, J. S. Thompson, *Inorg. Chem.* **1989**, *28*, 1091.

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