Inorganic Chemistry

Article

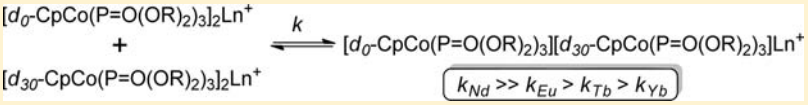
pubs.acs.org/IC

Lanthanide Complexes of the Kläui Metalloligand, $CpCo(P{=}O(OR)_2)_3$: An Examination of Ligand Exchange Kinetics between Isotopomers by Electrospray Mass Spectrometry

Kevin J. H. Allen, Emma C. Nicholls-Allison, Kevin R. D. Johnson, Rajinder S. Nirwan, David J. Berg,* Dennis Wester,† and Brendan Twamley‡

Department of Chemistry, University of Victoria, P.O. Box 3065, Victoria, British Columbia, Canada V8W 3V6

Supporting Information



ABSTRACT: A series of lanthanide complexes, $\{[CpCo(P{=}O(OR)_2)_3]_2Ln(H_2O)_x\}^+Cl^-$ (Ln = Nd, **3**; Eu, **4**; Tb, **5**; Yb, **6**; R = Et, **a**; R = Ph, **b**) bearing two cobalt metalloligands were prepared. Electrospray mass spectrometry and thermogravimetric analysis suggest that the cations are either solvent-free or contain very weakly bound water molecules. The related complex $\{[CpCo(P{=}O(OPh)_2)_3]_2Yb\}^+$ $[CoCl_3(THF)]^-$, **7**, was crystallographically characterized, and the cation in this case was confirmed to be 6-coordinate and solvent-free. Ligand exchange rates between the d_0- and d_{60}-isotopomers of **3a**–**6a** and **5b** were determined in acetonitrile by electrospray mass spectrometry. The ligand exchange rate was found to increase by almost 4 orders of magnitude from the smallest (Yb, **6a**, $k = 0.3\ M^{-1}\ s^{-1}$) to largest ion (Nd, **3a**, >2500 $M^{-1}\ s^{-1}$) in acetonitrile. Additionally, the ligand exchange rate increased rapidly for **5a** (Tb) with increasing water concentration from 30 $M^{-1}\ s^{-1}$ in pure acetonitrile to 268 $M^{-1}\ s^{-1}$ in 50:50 (v/v) acetonitrile/water. Changing the phosphite substituent had no significant impact on the rate of ligand exchange for **5b** (R = Ph) relative to **5a** (R = Et).

INTRODUCTION

The cobalt metalloligands, $[CpCo(P{=}O(OR)_2)_3]^-$, developed by Kläui function as tripodal oxygen donors to a wide variety of metals.[1] These ligands exhibit a number of interesting properties that make them attractive for *in vivo* studies including exceptionally high stability to oxidizing agents, water, and aqueous acids.[1,2] The solubility of the ligands in water or polar organic solvents can also be tuned by changing the phosphite substituents. We are interested in developing new lanthanide contrast agents for magnetic resonance imaging that are not based on the polyacetate DOTA-type structure.[3] The high affinity of lanthanides for oxygen donors and the exceptional stability of the Kläui metalloligands suggested that these ligands might provide a suitable platform to develop new contrast agents.

Lanthanide complexes of Kläui metalloligands, L_{CoP}, have been reported in the past. Included in this group are a number of mono(ligand) complexes such as $(L_{CoP})Ln(por)$ (Ln = Nd, Er, Yb, Y; por = various porphyrin derivatives),[4] $(L_{CoP})Y(H_2Bpz_2)$,[5] clusters with molybdenum oxo anions,[6] and acetate-bridged dimers $[(L_{CoP})Ln]_2(\mu\text{-}CH_3CO_2)_4$ (Ln = Nd, Y).[7] Among the bis(ligand) complexes, both neutral complexes such as $(L_{CoP})_2Ln(X)$ (X = acac, Cr_2O_7, $CH_3CO_2^-$)[8] and salts such as $[(L_{CoP})_2Ln(OH_2)_n]^+X^-$ (Ln = Eu, La; n = 1, 2; X = BF_4^-, Cl^-)[9] have been structurally characterized. Of these, the latter are expected to have the greatest water solubility and most potential as contrast agents, particularly since they have water molecules bound to the metal center.

In this contribution, we report the synthesis of several lanthanide complexes of the type $[(L_{CoP})_2Ln]^+Cl^-$ (Ln = Nd, Eu, Tb, Yb) that appear to be either solvent-free or to contain very weakly bound water molecules. We have verified crystallographically that the complex $[(L_{CoP})_2Ln]^+$ $[CoCl_3(THF)]^-$ contains a 6-coordinate cation without bound waters. Additionally, since lanthanide complexes of the Kläui metalloligand must show relatively low kinetic lability in aqueous solution to be useful as contrast agents, we investigated the rate of intermetallic ligand exchange between isotopomers using electrospray mass spectrometry. To the best of our knowledge, this is the first reported use of ESI MS to determine ligand exchange rates in lanthanide chemistry.[10]

RESULTS AND DISCUSSION

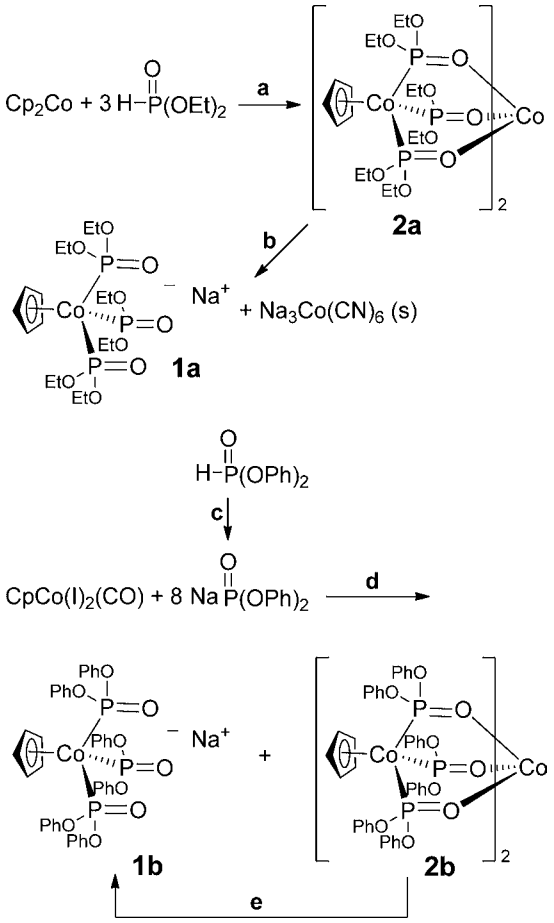
The Kläui ligands, $[CpCo(P{=}O(OR)_2)_3]^-$ were prepared as their sodium salts from Cp_2Co or $CpCo(CO)(I)_2$ using modified literature procedures, for **1a** (R = Et) and **1b** (R = Ph), respectively (Scheme 1).[11] Any of the paramagnetic trinuclear cobalt species, $[CpCo(P{=}O(OR)_2)_3]_2Co$, that formed were conveniently cleaved by reflux with NaCN in methanol.

Reaction of 2 equiv of the Na^+ salts of **1a** or **1b** with 1 equiv of $LnCl_3(H_2O)_n$ (n = 7, Ln = Nd; n = 6, Ln = Eu, Tb, Yb) in THF afforded the bis(ligand) complexes, $\{[CpCo(P{=}O-$

Received: August 21, 2012
Published: October 26, 2012

   dx.doi.org/10.1021/ic301830u | *Inorg. Chem.* 2012, 51, 12436–12443

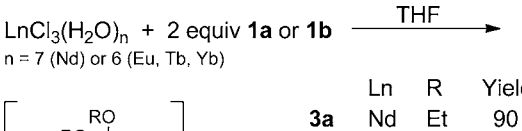
Scheme 1. Synthesis of Ligands, $[CpCo(P{=}O(OR)_2)_3]^-Na^+$, 1a (R = Et) and 1b (R = Ph)[a]



[a]Conditions: (a) 130 °C, 18 h, 78% yield; (b) NaCN, MeOH, reflux in air, 18 h, 95% yield; (c) NaH, THF, 0 °C; (d) reflux, THF, 18 h, 73% yield; (e) NaCN, toluene−MeOH, reflux in air, 18 h.

$(OR)_2)_3]_2Ln(H_2O)_x\}^+Cl^-$ (Ln = Nd, **3**; Eu, **4**; Tb, **5**; Yb, **6**; R = Et, **a**; R = Ph, **b**) as microcrystalline solids (Scheme 2). The

Scheme 2. Synthesis of Lanthanide Complexes, $\{[CpCo(P{=}O(OR)_2)_3]_2Ln\}^+ Cl^-$



	Ln	R	Yield %
3a	Nd	Et	90
3b	Nd	Ph	91
4a	Eu	Et	82
5a	Tb	Et	73
5b	Tb	Ph	85
6a	Yb	Et	83
6b	Yb	Ph	93

water content of these complexes varies from 2 to more than 20 equiv, but the average value for most complexes is about 8 equiv of water. Most samples remain hydrated with 2−4 waters after exposure to vacuum at room temperature.

Thermogravimetric analysis of complex **3a** shows a steady loss of ca. 4 water molecules until the anhydrous complex is reached at 65 °C. Anhydrous **3a** remains stable until about 185 °C at which point it loses mass consistent with the loss of ethyl chloride (or ethene and HCl); steady mass loss due to further decomposition occurs beyond 210 °C. A TGA of **5a** (Ln = Tb) shows very similar behavior with loss of ca. 2 water molecules by ca. 65 °C and loss of ethyl chloride beginning at only 135 °C. Presumably greater steric crowding at the smaller Tb^{3+} center in **5a** destabilizes the complex relative to Nd^{3+} complex **5a**. Interestingly, Nolan et al. reported a neutral, dimeric complex, $\{[CpCo(P{=}O(OEt)_2)_3][\mu\text{-}CpCo(P{=}O(OEt)_2)_2(P(O)_2(OEt)]Y\}_2$ containing one bridging $[CpCo(P{=}O(OEt)_2)(PO_2(OEt)]^{2-}$ ligand.[12] The authors obtained this complex by refluxing the Na^+ salt of **1a** with anhydrous YCl_3 in THF and given the low temperature required for loss of ethyl chloride from **3a** and **5a** by TGA, it is reasonable to speculate that ligand fragmentation occurs after complex formation at the temperatures used.

The phenyl-substituted complex **6b** (Ln = Yb) also shows low-temperature loss of two water molecules (complete by 50 °C), but in this case, the anhydrous complex remains stable to more than 220 °C. Above this temperature, there is a clear mass loss consistent with loss of a phosphite arm ($O{=}P(OPh)_2$) followed by further decomposition at temperatures above 250 °C. The ease with which these complexes dehydrate on heating during TGA strongly suggests that the water molecules present are not bonded to the metal ions. This is confirmed crystallographically for the $\{[CpCo(P{=}O(OPh)_2)_3]_2Yb\}^+$ cation in **7** discussed below.

During the initial synthesis of yellow microcrystalline **6b**, a small amount of green X-ray quality crystals were obtained that correspond to the expected $\{[CpCo(P{=}O(OPh)_2)_3]_2Yb\}^+$ cation with a tetrahedral $\{CoCl_3(THF)\}^-$ counterion, **7**. Recrystallization of **7** from acetone containing NaCl resulted in a pale yellow solid corresponding to **6b**. Complex **7** shows absorptions at 592, 623, and 684 (ε = 22 L mol^{-1} cm^{-1}) which are consistent with the blue, distorted tetrahedral $[CoCl_3(THF)]^-$ anion;[13] **6b** on the other hand shows only a peak tailing into the visible at ca. 400 nm.

An ORTEP3 plot[14] of **7** is shown in Figure 1, while selected bond distance and angles are collected in Table 1. At this

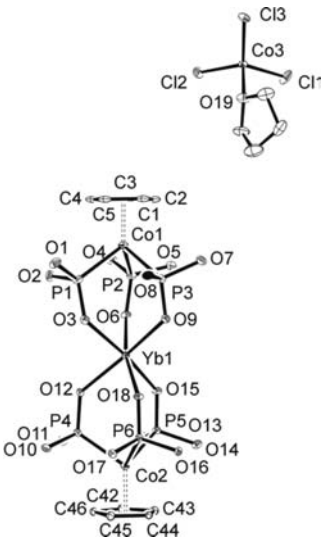


Figure 1. ORTEP3[14] plot of $\{[CpCo(P{=}O(OPh)_2)_3]_2Yb\}^+ \{CoCl_3(THF)\}^-\cdot 2C_6H_6$, **7** (50% probability ellipsoids; phosphite phenyl groups and benzenes of solvation omitted for clarity).

dx.doi.org/10.1021/ic301830u | Inorg. Chem. 2012, 51, 12436−12443

Table 1. Selected Bond Lengths and Angles for $\{[CpCo(P{=}O(OPh)_2)_3]_2Yb\}^+$ $\{CoCl_3(THF)\}^-\cdot 2C_6H_6$, 7[a]

			Cation		
Yb(1)−O(3)	2.227(4)	Yb(1)−O(6)	2.207(4)	Yb(1)−O(9)	2.213(4)
Yb(1)−O(12)	2.220(4)	Yb(1)−O(15)	2.205(4)	Yb(1)−O(18)	2.207(4)
P(1)−O(3)	1.512(5)	P(2)−O(6)	1.521(5)	P(3)−O(9)	1.517(5)
P(4)−O(12)	1.509(5)	P(5)−O(15)	1.506(4)	P(6)−O(18)	1.502(5)
Co(1)−P(1)	2.160(2)	Co(1)−P(2)	2.150(2)	Co(1)−P(3)	2.159(2)
Co(2)−P(4)	2.161(2)	Co(2)−P(5)	2.162(2)	Co(2)−P(6)	2.171(2)
Co(1)-Cp(1)[b]	1.694	Co(2)−Cp(2)[b]	1.736	$Co(1)-C(Cp1)_{ave}$[c]	2.075
$Co(1)-C(Cp2)_{ave}$[c]	2.110				
Yb(1)−O(3)−P(1)	128.3(3)	Yb(1)−O(6)−P(2)	131.1(3)	Yb(1)−O(9)−P(3)	128.4(3)
Yb(1)−O(12)−P(4)	132.7(3)	Yb(1)−O(15)−P(5)	132.6(2)	Yb(1)−O(18)−P(6)	133.5(3)
Co(1)−P(1)−O(3)	118.9(2)	Co(1)−P(2)−O(6)	119.2(2)	Co(1)−P(3)−O(9)	120.0(2)
Co(2)−P(4)−O(12)	119.8(2)	Co(2)−P(5)−O(15)	120.1(2)	Co(2)−P(6)−O(18)	119.3(2)
			Anion		
Co(3)−Cl(1)	2.245(2)	Co(3)−Cl(2)	2.223(2)	Co(3)−Cl(3)	2.238(2)
Co(3)−O(19)	2.037(5)				
Cl(1)−Co(3)−Cl(2)	113.56(11)	Cl(1)−Co(3)−Cl(3)	117.44(11)	Cl(1)−Co(3)−O(19)	102.3(2)
Cl(2)−Co(3)−Cl(3)	113.3(10)	Cl(2)−Co(3)−O(19)	105.7(2)	Cl(3)−Co(3)−O(19)	102.4(2)

[a]Estimated standard deviation in parentheses. [b]Cp designated the centroid of the cyclopentadienyl C_5 ring. [c]Average distance from cobalt to the cyclopentadienyl ring carbons.

writing, there are 24 reports of crystallographically characterized lanthanide complexes containing Kläui ligands, although in all cases, the phosphite substituents are aliphatic, making this the first example of an aryl substituted Kläui lanthanide complex.[4−9] The bond lengths within the Kläui ligand of **7** are unremarkable; however, the Yb−O distances are at the long end of the range of distances in the previously reported complexes after adjustment for lanthanide ionic radius and coordination number (lit:[4−9] 2.10−2.24 Å, mean = 2.17 Å; **7**: 2.205(4)−2.227(4) Å, mean = 2.213 Å). This observation, the fact that **7** is the only six-coordinate complex containing two Kläui ligands and the lack of chloride or water coordination, suggests that the ytterbium center in **7** is relatively crowded.

The solid state structure of **7** suggested that complexes **3**−**6** also exist as salts containing a $\{[CpCo(P{=}O(OR)_2)_3]_2Ln\}^+$ cation. Indeed, electrospray MS in positive ion mode from acetonitrile or a mixture of acetonitrile and water readily gave the expected isotopic pattern for the intact cation as shown, for example, for **3a** in Figure 2. No higher mass peaks were observed, suggesting that the cations are not solvated, at least under ESI MS conditions.

The utility of complexes like **3**−**6** as possible MRI relaxation agents depends, in part, on the lability of the Kläui metalloligand in aqueous solution at blood pH (ca. 7.4).[3,15] Although we expected the unmodified Kläui ligands used here to be quite labile, there is no information available in the literature regarding the lability of a tridentate ligand set such as that presented by a Kläui ligand. Therefore, to provide a baseline for any future work, we set out to determine the lability of the ligands used here as a function of metal size and ligand substituent. In addition, since these complexes are only soluble in polar solvents containing limited amounts of water, we also examined how increasing water in a polar solvent changes the rate of ligand exchange.

The ease with which we obtained a mass spectrum for the cations of **3**−**6** by positive ESI suggested a straightforward method to measure the rate of ligand exchange. The Kläui ligands were easily deuterated at every position except the cyclopentadienyl ring by using either d_6-ethanol or d_6-phenol when preparing the phosphite. In both cases, this allows

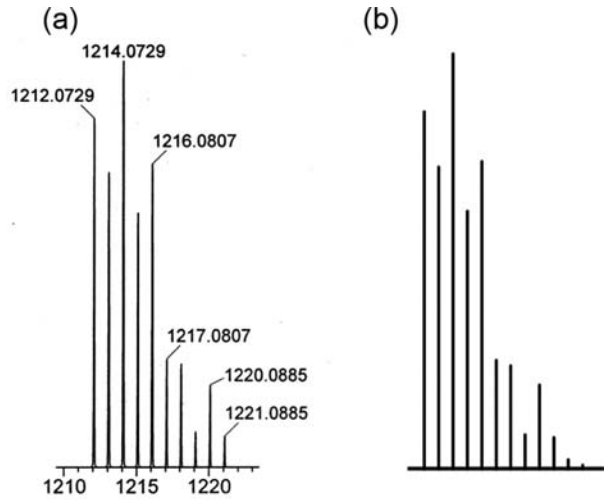


Figure 2. Observed (a) and simulated (b) isotopic distribution for the cation, $\{[CpCo(P{=}O(OEt)_2)_3]_2Nd\}^+$, of **3a**.

formation of the d_{30}-$[CpCo(P{=}O(OR)_2)_3]^-$ ligand from which the corresponding d_{60}-$\{[CpCo(P{=}O(OR)_2)_3]_2Ln\}^+$ analogues of **3**−**6** were prepared. The ligand exchange reaction was followed by mixing equimolar amounts of d_0 **3**−**6** with their d_{60} analogues in acetonitrile and following the rate of disappearance of either the d_0 or d_{60} cation or the appearance of the d_{30} ligand exchange product with time as illustrated in Figure 3 for $\{[CpCo(P{=}O(OEt)_2)_3]_2Tb\}^+$ Cl^-, **5a**.[16]

The reaction between the d_0- and d_{60}-$\{[CpCo(P{=}O(OR)_2)_3]_2Ln\}^+$ complexes follow first-order behavior in each complex (2nd order overall), so a plot of $1/[d_{60}]$ or $1/[d_0]$ versus time initially follows a straight line of slope k. Good linear behavior is observed until at least 25% conversion, but eventually, the back reaction becomes significant and the apparent rate declines (Figure 4). As expected, the reaction mixture eventually reaches a thermodynamic 1:2:1 mixture of d_0:d_{30}:d_{60} isotopomers (Figure 3).

dx.doi.org/10.1021/ic301830u | Inorg. Chem. 2012, 51, 12436−12443

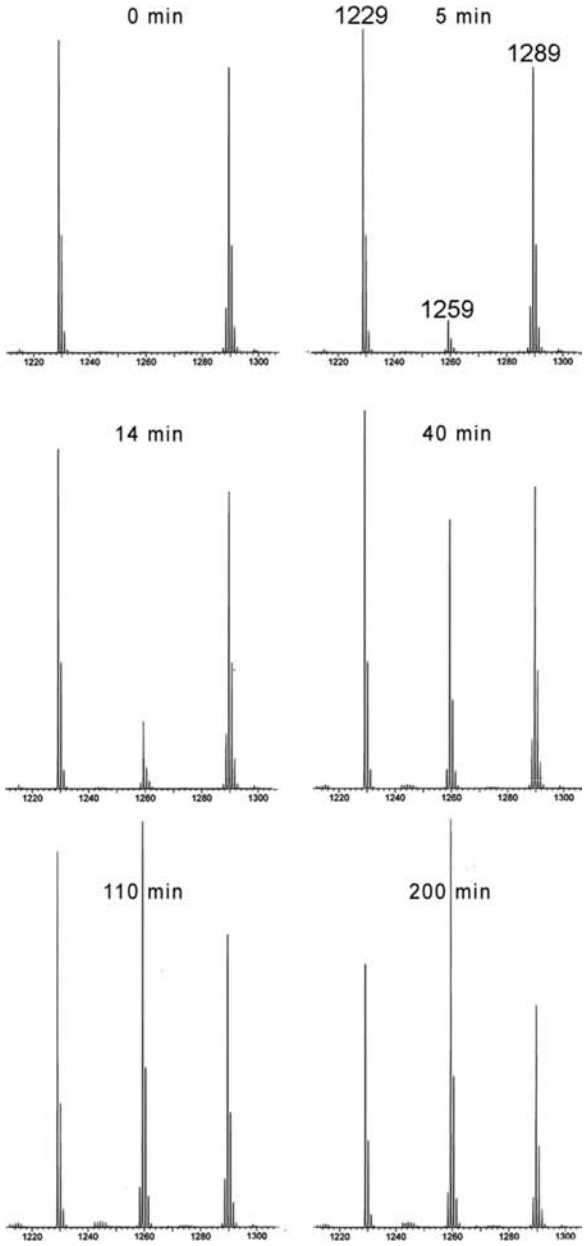


Figure 3. Electrospray mass spectra (positive mode, acetonitrile) showing the evolution of the d_0, d_{30}, and d_{60} isotopic manifolds over time for the cation of $\{[CpCo(P{=}O(OEt)_2)_3]_2Tb\}^+$ Cl^-, **5a**, after mixing equimolar amounts of the d_0- and d_{60}-isotopomers (7.905×10^{-6} M).

The observed rate constants for ligand exchange derived from electrospray MS are summarized in Table 2. We estimate an error of roughly 10% in these values based on the reproducibility between runs. Obviously, our ability to handle very fast reactions is limited by the time required to mix the d_0- and d_{60}-isotopomers and inject them into the mass spectrometer (ca. 1–2 min). In the case of $\{[CpCo(P{=}O(OEt)_2)_3]_2Nd\}^+$ Cl^-, **3a**, this meant that we could only estimate a lower limit for the rate constant k. Fortunately, in most of the cases studied here, the rate was sufficiently slow that reliable values for k could be determined.

The rate constant for ligand exchange increases sharply as the ionic radius of the lanthanide increases (Figure 5).[17] In fact, a plot of log k vs lanthanide ionic radius in six-coordination is roughly linear (Figure 6). This observation is consistent with an associative mechanism where ligand exchange occurs within a dimeric aggregate through bridging interactions. The X-ray structure of the related neutral yttrium dimer, $\{[CpCo(P{=}O(OEt)_2)_3][\mu\text{-}CpCo(P{=}O(OEt)_2)_2(P(O)_2(OEt)]Y\}_2$, men-

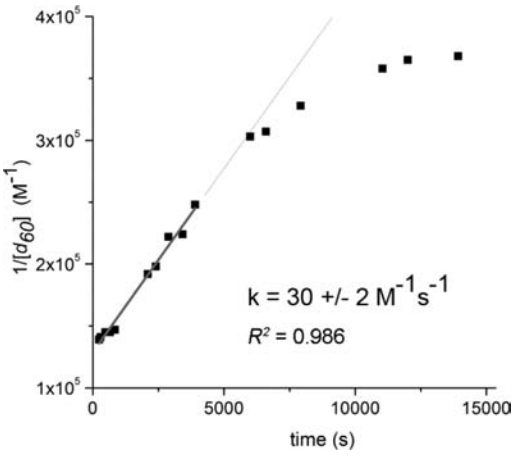


Figure 4. Plot of $1/[d_{60}\text{-}\mathbf{5a}]$ versus time for the reaction between d_0 and d_{60}-$\{[CpCo(P{=}O(OEt)_2)_3]_2Tb\}^+$ Cl^- (**5a**) in acetonitrile monitored by ESI MS (7.905×10^{-6} M each).

Table 2. Summary of Rate Constant Data for Ligand Exchange between d_0- and d_{60}-$\{[CpCo(P{=}O(OR)_2)_3]_2Ln\}^+$ Cl^-

compd	Ln	R	ACN/H_2O[a]	k (M^{-1} s^{-1})[b]
3a	Nd	Et	100:0	>2500
4a	Eu	Et	100:0	575
5a	Tb	Et	100:0	30
5a	Tb	Et	90:10	55
5a	Tb	Et	80:20	67
5a	Tb	Et	70:30	74
5a	Tb	Et	60:40	166
5a	Tb	Et	50:50	268
5b	Tb	Ph	100:0	34
5b	Tb	Ph	50:50	100
6a	Yb	Et	100:0	0.3
6a	Yb	Et	50:50	11

[a]Acetontrile/water ratio in v/v percentages. [b]Estimated error ca. 10%.

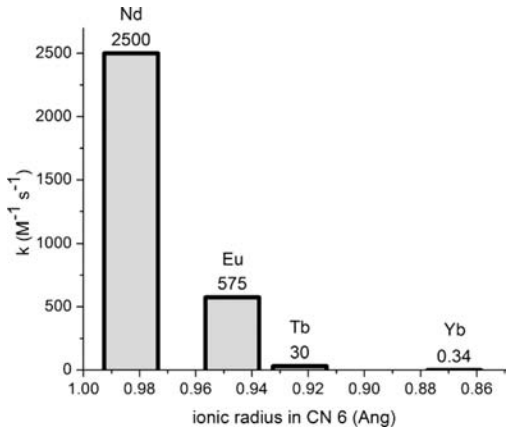


Figure 5. Plot of rate constant k versus ionic radius (Å) for the reaction between d_0 and d_{60}-$\{[CpCo(P{=}O(OEt)_2)_3]_2Ln\}^+$ Cl^- (**3a**–**6a**) in acetonitrile monitored by ESI MS.

dx.doi.org/10.1021/ic301830u | Inorg. Chem. 2012, 51, 12436–12443

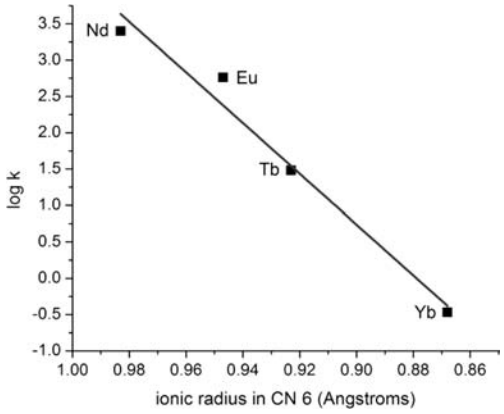


Figure 6. Plot of log k versus ionic radius (Å) for the reaction between d_0 and d_{60}-{[CpCo(P═O(OEt)$_2$)$_3$]$_2$Ln}$^+$ Cl$^-$ (**3a**–**6a**) in acetonitrile monitored by ESI MS.

tioned above, is noteworthy in this regard because it shows that dimer formation is feasible in a similar system.[12] Although there are no structurally characterized examples of intact [CpCo(P═O(OEt)$_2$)$_3$]$^-$ units bridging two lanthanide centers, it is reasonable to assume that such a dimer could form, particularly if one P═O arm dissociates from the lanthanide center.

Addition of water to the acetonitrile solvent was investigated to the limit of solubility (ca. 50% water) in the case of the Tb complexes **5a** and **5b**. The rate of exchange increased rapidly with increasing water content in the solvent, as illustrated for **5a** in Figure 7. Overall, the rate constant increased about 8-fold for

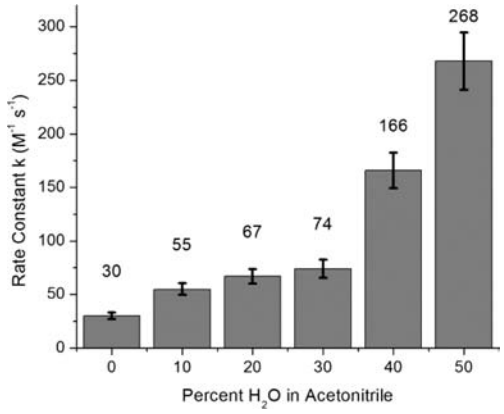


Figure 7. Plot of rate constant k versus water content (v/v) for the reaction between d_0 and d_{60}-{[CpCo(P═O(OEt)$_2$)$_3$]$_2$Tb}$^+$ Cl$^-$ (**5a**) in acetonitrile monitored by ESI MS.

the Et complex **5a** and about 3-fold for the Ph complex **5b** on going from pure acetonitrile to a 50:50 acetonitrile/water mixture. The reason for this strong water dependence is not clear, but it could be that water competes with P═O binding and dissociation of one arm of the Kläui ligand facilitates bridge formation. We have not investigated the effect of changing pH on the rate of exchange, but it is quite likely that labile hydroxo bridges could form at slightly basic pH and that these could facilitate dimer formation.

There does not appear to be a strong rate dependence on the phosphite substituent. The rate constants for the Et and Ph complexes of Tb, **5a** and **5b**, are essentially the same within experimental error in pure acetonitrile, although **5a** is noticeably faster in 50:50 acetonitrile/water (ca. 2.7 times). This is not surprising if steric effects dominate the exchange process, because the substituents are relatively far away from the metal center and the size differences between an Et and Ph group are not that extreme. On the other hand, Kläui and coworkers have found that changing from Et to Ph causes a change from a dimeric [CpCo(P═O(OEt)$_2$)$_3$]$_2$Rh$_2$(CO)$_3$ to a monomeric [CpCo(P═O(OPh)$_2$)$_3$]Rh(CO)$_2$.[18]

CONCLUDING REMARKS

We have shown that the complexes {[CpCo(P═O(OR)$_2$)$_3$]$_2$Ln}$^+$ Cl$^-$ (R = Et, Ph) are isolated as salts with good solubility in acetonitrile and limited solubility in water. Intramolecular ligand exchange was followed by ESI MS using the d_0- and d_{60}-isotopomers of the cation. The kinetic results are consistent with an associative process. The rate of exchange increases rapidly with increasing lanthanide ionic radius and water content, but the phosphite substituents have comparatively little effect. The rate of ligand exchange is sufficiently high that lanthanide complexes of the simple [CpCo(P═O(OR)$_2$)$_3$]$^-$ ligands are not likely to be suitable for medical uses; however, incorporating chelating functionality into the phosphite groups may lower the ligand exchange rate to an acceptable level, especially for complexes of the later lanthanides.

EXPERIMENTAL SECTION

All experiments were performed under an inert argon atmosphere using standard glovebox (Braun MB150-GII) or Schlenk techniques in flame-dried glassware unless otherwise noted. THF and ether were freshly distilled from sodium/benzophenone before use; dichloromethane was distilled from calcium hydride unless stated otherwise. CpCo(I)$_2$CO was synthesized from commercially available (Aldrich) CpCo(CO)$_2$ according to the literature procedure.[19] The deuterated phosphites d_{10}-diethylphosphite and d_{10}-diphenylphosphite were prepared from PCl$_3$ in two steps: initial reaction of PCl$_3$ with *t*-butanol (1 equiv) followed by addition of commercially available d_6-ethanol or d_6-phenol (2 equiv) by a modification of a literature procedure.[20] Acetonitrile for ESI MS studies was HPLC grade. All other chemicals were purchased from Sigma-Aldrich and used as is. Samples for NMR spectroscopy were recorded on Bruker AMX-300 MHz or 360 MHz NMR. FT-IR spectra were recorded on a Perkin-Elmer Spectrum 1000 FT-IR. An Omega Engineering model 199 melting point apparatus was used for melting point data. Kinetic +ESI-MS data was collected on a Q-TOF II by MicroMass.

Table 3. Summary of Crystallographic Data for 7

formula	$C_{98}H_{90}Cl_3Co_3O_{19}P_6Yb$
fw	2213.70
cryst syst	orthorhombic
space group	$P2_12_12_1$ (no. 19)
a (Å)	19.6632(7)
b (Å)	19.7358(7)
c (Å)	24.5563(9)
V (Å^3)	9529.5(6)
Z	4
ρ_{calc} (g cm^{-3})	1.543
μ (mm^{-1})	1.739
$2\theta_{max}$ (deg)	50.5
meas. refl.	123863
unique refl.	17278
R^a, $R_w{}^b$	0.048, 0.101
GOF	1.023

$^aR = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. $^bR_w = [\Sigma w(|F_o| - |F_c|^2)/\Sigma w(|F_o|)^2]^{1/2}$.

dx.doi.org/10.1021/ic301830u | *Inorg. Chem.* 2012, 51, 12436–12443

Synthesis. *O═P(H)(OC$_2$D$_5$)$_2$.* Anhydrous *t*-butanol (3.5 g, 48.0 mmol) was dissolved in dichloromethane (10 mL) and the mixture was added to freshly distilled PCl_3 (6.59 g, 48.0 mmol) dissolved in dichloromethane (50 mL) at 0 °C. The solution was stirred 1 h, then allowed to warm to room temperature, and deuterated ethanol (5.0 g, 96 mmol) was added dropwise over 0.5 h. This solution was stirred for 1.5 h at room temperature and then refluxed for 18 h. Removal of the solvent under reduced pressure and vacuum distillation afforded pure deuterated diethylphosphite as a clear and colorless oil. Yield: 5.3 g (75%). ^{1}H NMR ($CDCl_3$, 300 MHz, 22 °C): δ 6.79 (d, 1H, $^1J_{PH}$ = 694 Hz, 1H). ^{31}P{^{1}H} NMR (121.5 MHz): δ 6.43 s.

O═P(H)(OC$_6$D$_5$)$_2$. Anhydrous *t*-butanol (1.85 g, 24.96 mmol) dissolved in 10 mL dichloromethane was added to freshly distilled PCl_3 (3.43g, 24.96 mmol) dissolved in dichloromethane (30 mL) at 0 °C. The solution was stirred for 1 h, then allowed to warm to room temperature. Deuterated phenol (5.0 g, 49.92 mmol) dissolved in dichloromethane (30 mL) was added dropwise over 0.5 h, and the solution stirred for 1.5 h at room temperature and then refluxed for 18 h. Removal of the solvent under reduced pressure left a yellow oil containing up to 5% of the monoaryl substituted phosphite as a contaminant. The crude product was redissolved in dichloromethane (30 mL) and ammonia was bubbled through the solution for 10 min resulting in a milky white suspension. Filtration through Celite and removal of the solvent under reduced pressure afforded pure deuterated diphenylphosphite as a clear colorless oil. Yield: 5.43 g (89%). ^{1}H NMR (CD_2Cl_2, 300 MHz, 22 °C): δ 7.34 (d, 1H, $^1J_{PH}$ = 732 Hz). ^{31}P{^{1}H} NMR (CD_2Cl_2, 121.5 MHz): δ 0.91 s.

[CpCo(P═O(OEt)$_2$)$_3$]$^-$ Na$^+$, ***1a.*** Solid NaCN (0.95 g, 19.3 mmol) was added to a slurry of **2a** (3.57g, 3.20 mmol), described below, in 30 mL methanol. The mixture was refluxed in air for 18 h, and the solution cooled to room temperature, filtered through Celite, and washed with dichloromethane leaving behind insoluble $Na_3[Co(CN)_6]$. The filtrate was evaporated to dryness under reduced pressure and the residue was recrystallized from hot acetone to yield pure **1a**. Yield: 3.21 g (95%). Mp. 188−189 °C. IR (thin film, NaCl): 2974m, 2927w, 2894w, 1384w, 1161s, 1047s, 929s, 830w, 759m, 723m cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz, 22 °C): δ 4.99 (s, 5H, C_5H_5), 3.98−3.89 (m, 12H, CH_2), 1.21 (t, $^3J_{HH}$ = 7.3 Hz, 18H, CH_3). ^{31}P{^{1}H} NMR ($CDCl_3$, 121.5 MHz): δ 105.89 s. ^{13}C{^{1}H}($CDCl_3$, 75.5 MHz): δ 89.67 (s, C_5H_5), 58.64 (m, CH_2), 16.70 (s, CH_3).

[CpCo(P═O(OC$_2$D$_5$)$_2$)$_3$]$^-$ Na$^+$, d$_{30}$- ***1a.*** The deuterated complex was prepared in the same manner as **1a** from NaCN and d_{60}-**2a**. Yield: 2.06 g (99%). Mp 188−190 °C. IR (thin film, NaCl): 2224m, 2144w, 2101w, 1426w, 1183s, 1163s, 1099m, 1061m, 1007s, 908w, 814m, 733w, 687m, 667m cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz, 22 °C) δ 4.96 (s, C_5H_5). ^{2}H NMR ($CHCl_3$, 55.3 MHz): δ 3.93 (s, 12D, CD_2), 5.56 (s, 18D, CD_3). ^{31}P{^{1}H} NMR ($CDCl_3$, 121.5 MHz): δ 105.66 s. ^{13}C{^{1}H} NMR ($CDCl_3$, 75.5 MHz): δ 89.60 (s, C_5H_5), 57.74 (quin, $^1J_{CD}$ = 21 Hz, CD_2), 15.62 (sept, $^1J_{CD}$ = 20 Hz, CD_3).

[CpCo(P═O(OPh)$_2$)$_3$]$^-$ Na$^+$, ***1b.*** A solution of diphenylphosphite (7.65 g, 32.7 mmol) in freshly distilled THF (100 mL) was added dropwise to a slurry of NaH (0.98g, 60% dispersion in mineral oil, 24.5 mmol) in THF (60 mL) at 0 °C. This suspension was stirred for 0.5 h at 0 °C and then allowed to warm to room temperature. $CpCo(I)_2CO$ (1.70 g, 4.19 mmol) dissolved in THF (50 mL) was then added dropwise over 1 h resulting in an orange solution. The orange solution was allowed to stir for 1 h and then refluxed for 18 h. After cooling to room temperature, a small amount of water was added to quench the reaction and the solvent was removed under reduced pressure leaving an orange solid. The orange residue was dispersed in hexanes, filtered, and the solid washed with water (50 mL), followed by cold methanol (50 mL) to leave crude **1b** as a yellow powder. ^{1}H NMR revealed ∼5% impurity consistent with the presence of $[CpCo(P{=}O(OPh)_2)_3]_2Co$, **2b**. To remove this impurity, the crude product was dissolved in a mixture of toluene (50 mL) and methanol (10 mL) containing NaCN (0.05 g) and the mixture was refluxed in air overnight. After filtration through Celite to remove any unreacted NaCN and insoluble $Na_3[Co(CN)_6]$, pure **1b** was recovered as a yellow solid. Yield: 3.37 g (73%). Mp. 302 °C (dec). IR (thin film, NaCl): 3065w, 1591s, 1489s, 1213s, 1193m, 1157w, 1068w, 1023w 872s, 763w, 690m cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz, 22 °C) δ 6.85−6.77 (m, 30H, aryl*H*), 5.59 (s, 5H, C_5H_5). ^{31}P{^{1}H} NMR ($CDCl_3$, 121.5 MHz): δ 103.20 s. ^{13}C{^{1}H} NMR ($CDCl_3$, 75.5 MHz): δ 152.69 (m, *ipso*-aryl), 128.78 (s, *m*-aryl), 122.99 (s, *p*-aryl), 121.90 (s, *o*-aryl), 90.72 (s, C_5H_5).

[CpCo(P═O(OC$_6$D$_5$)$_2$)$_3$]$^-$ Na$^+$, d$_{30}$- ***1b.*** The same procedure was used to prepare d_{30}-**1b** as that used to prepare **1b** except that d_{10}-diphenylphosphite was used in place of diphenylphosphite. Yield: 1.13 g (46%). Mp. 311 °C (dec). IR (thin film, NaCl): 2276w, 1557s, 1375s, 1204m, 1156s, 1140s, 962w, 889m, 847m, 799s, 772w, 680w cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz, 22 °C): δ 5.59 (s, C_5H_5). ^{2}H ($CHCl_3$, 55.3 MHz): δ 7.02 (s, br, 30D, aryl*D*). ^{31}P{^{1}H} NMR ($CDCl_3$, 121.5 MHz): δ 102.57 s. ^{13}C{^{1}H} NMR ($CDCl_3$, 75.5 MHz): δ 152.65 (m, *ipso*-aryl), 128.78 (t, $^1J_{CD}$ = 22 Hz, *m*-aryl), 122.51 (t, $^1J_{CD}$ = 20 Hz, *p*-aryl), 121.56 (t, $^1J_{CD}$ = 22 Hz, *o*-aryl), 90.72 (s, C_5H_5).

[CpCo(P═O(OEt)$_2$)$_3$]$_2$Co, ***2a.*** Freshly sublimed cobaltocene (2.30 g, 12.2 mmol) was added to a Schlenk tube under an inert atmosphere and diethylphosphite (4.66 mL, 5.0 g, 36.2 mmol) was injected by syringe. The resulting mixture was heated at 130 °C for 18 h, cooled to room temperature, and diluted with 25 mL of methanol. After stirring for 0.5 h, the suspension was filtered to isolate **2a** as a pale yellow solid. Yield: 3.57 g (78%). Mp. 254−257 °C. IR (thin film, NaCl): 2973m, 2920w, 2892w, 1422w, 1385m, 1263s, 1126s, 1039s, 922s, 833w, 748m, 719m cm^{-1}. ^{1}H NMR ($CDCl_3$, 360 MHz, 22 °C): δ 33.84 (s, 10H, C_5H_5, $\nu_{1/2}$ = 21 Hz), −12.09 (s, 36H, CH_3, $\nu_{1/2}$ = 21 Hz), −23.00 (s, 12H, CH_AH_B, $\nu_{1/2}$ = 71 Hz), −29.43 (s, 12H, CH_AH_B, $\nu_{1/2}$ = 103 Hz).

[CpCo(P═O(OC$_2$D$_5$)$_2$)$_3$]$_2$Co, d$_{60}$- ***2a.*** The deuterated complex was prepared by the same procedure as for **2a** but with d_{10}-diethylphosphite substituted for diethylphosphite. Yield: 2.19 g (74%). Mp. 239−241 °C. IR (thin film, NaCl): 2224m, 2143w, 2101w, 1422w, 1265s, 1177s, 1135s, 1090s, 1060m, 1008s, 906w, 821m, 739s, 690w, 671w cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz, 22 °C): δ 33.78 (s, 10H, C_5H_5, $\nu_{1/2}$ = 20 Hz). ^{2}H NMR ($CHCl_3$, 55.3 MHz): δ −11.99 (s, 36H, CH_3, $\nu_{1/2}$ = 7 Hz), −22.37 (s, 12H, CH_AH_B, $\nu_{1/2}$ = 13 Hz), −28.80 (s, 12H, CH_AH_B, $\nu_{1/2}$ = 12 Hz).

{[CpCo(P═O(OEt)$_2$)$_3$]$_2$Nd}$^+$ Cl$^-$, ***3a.*** The ligand salt **1a** (0.40g, 0.72 mmol) and $NdCl_3(H_2O)_7$ (0.139g, 0.36 mmol) were stirred in 20 mL reagent-grade THF in air for 18 h. The solution was filtered through Celite and the solvent was removed to leave a yellow solid. The solid was redissolved in dichloromethane, filtered through Celite once more, and the filtrate evaporated to dryness. The residue was redissolved in a minimum of dichloromethane and precipitated with hexanes to afford **3a** as a yellow solid. Yield: 0.23 g (90%). Mp. 188−190 °C. IR (thin film, NaCl): 2976m, 2927w, 2898w, 1385w, 1125s, 1041s, 933s, 832w, 769w, 727w cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz, 22 °C): δ 10.40 (s, 10H, C_5H_5, $\nu_{1/2}$ = 8 Hz), 2.05 (s, CH_AH_B, $\nu_{1/2}$ = 29 Hz), 1.79 (s, 12H, CH_AH_B, $\nu_{1/2}$ = 28 Hz), −0.15 (s, 36H, CH_3, $\nu_{1/2}$ = 18 Hz), −2.54 (s, ∼12 equiv H_2O, $\nu_{1/2}$ = 19 Hz). ^{31}P{^{1}H} NMR ($CDCl_3$, 121.5 MHz): δ −189.45 (s, $\nu_{1/2}$ = 72 Hz).

{[CpCo(P═O(OC$_2$D$_5$)$_2$)$_3$]$_2$Nd}$^+$ Cl$^-$, d$_{60}$- ***3a.*** The deuterated complex was prepared according to the same procedure as **3a** using d_{30}-**1a** instead of **1a**. Yield: 0.102 g (84%). Mp. 177−178 °C. IR (thin film, NaCl): 2226s, 2143m, 2102m, 1425w, 1187s, 1133s, 1086s, 1059s, 1008s, 928m, 829s, 731w, 683m, 673m cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz, 22 °C): δ 10.44 (s, C_5H_5, $\nu_{1/2}$ = 7 Hz), −10.53 (s, ∼4 equiv H_2O, $\nu_{1/2}$ = 51 Hz). ^{2}H NMR ($CHCl_3$, 55.3 MHz): δ 2.06 (s, 12D, CD_AD_B, $\nu_{1/2}$ = 4 Hz), 1.74 (s, 12D, CD_AD_B, $\nu_{1/2}$ = 5 Hz), −0.15 (s, 36D, CD_3, $\nu_{1/2}$ = 3 Hz). ^{31}P{^{1}H} NMR ($CDCl_3$, 121.5 MHz): δ −189.33 (s, $\nu_{1/2}$ = 66 Hz).

{[CpCo(P═O(OPh)$_2$)$_3$]$_2$Nd}$^+$ Cl$^-$, ***3b.*** Complex **3b** was prepared as a yellow solid using the same procedure as **3a** but starting from **1b** and $NdCl_3(H_2O)_7$. Yield: 0.356 g (91%). Mp. 291 °C (dec). IR (thin film, NaCl): 3065w, 1589s, 1488s, 1208s, 1183m, 1163m, 1134s, 1071w, 1024w, 910s, 888s, 847w, 757m, 689m cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz, 22 °C): δ 10.48 (s, 10H, C_5H_5, $\nu_{1/2}$ = 8 Hz), 5.38 (s, 12H, *p*-aryl*H*, $\nu_{1/2}$ = 9 Hz), 4.88 (s, 24H, *o*/*m*-aryl*H*, $\nu_{1/2}$ = 21 Hz), 3.96 (s, 24H, *o*/*m*-aryl*H*, $\nu_{1/2}$ = 20 Hz), −3.99 (s, 7 equiv H_2O, $\nu_{1/2}$ = 45 Hz). ^{31}P{^{1}H} NMR ($CDCl_3$, 121.5 MHz): δ 195.40 (s, $\nu_{1/2}$ = 55 Hz).

dx.doi.org/10.1021/ic301830u | *Inorg. Chem.* 2012, 51, 12436−12443

{[CpCo(P═O(OC$_6$D$_5$)$_2$)$_3$]$_2$Nd}$^+$ Cl$^-$, *d$_{60}$-**3b***. The deuterated complex was prepared according to the same procedure as **3a** using *d*$_{30}$-**1b** instead of **1a**. Yield: 0.091 g (85%). Mp. 285 °C (dec). IR (thin film, NaCl): 2277w, 1556s, 1372s, 1155s, 1132s, 964w, 898s, 853m, 804s, 770w, 703w cm^{-1}. ^{1}H NMR (CDCl$_3$, 300 MHz, 22 °C): δ 10.61 (s, C$_S$*H*$_S$, $\nu_{1/2}$ = 8 Hz), −7.62 (s, 4 equiv H$_2$O, $\nu_{1/2}$ = 143 Hz). ^{31}P{^{1}H} NMR (CDCl$_3$, 121.5 MHz): δ 194.79 (s, $\nu_{1/2}$ = 56 Hz).

{[CpCo(P═O(OEt)$_2$)$_3$]$_2$Eu}$^+$ Cl$^-$, ***4a***. Complex **4a** was isolated as a yellow solid using the same procedure as **3a** starting from **1a** and EuCl$_3$(H$_2$O)$_6$. Yield: 0.21 g (82%). Mp. 158−160 °C. IR (thin film, NaCl): 2976m, 2927w, 2899w, 1386w, 1125s 1040s, 934s, 832w, 770w, 727w cm^{-1}. ^{1}H NMR (CDCl$_3$, 300 MHz, 22 °C): δ 5.95 (s, 12H, C*H*$_A$H$_B$, $\nu_{1/2}$ = 24 Hz), 5.64 (s, 12H, CH$_A$*H*$_B$, $\nu_{1/2}$ = 26 Hz), 2.96 (s, ∼30 equiv H$_2$O, $\nu_{1/2}$ = 10 Hz), 2.45 (s, 36H, C*H*$_3$, $\nu_{1/2}$ = 13 Hz), 0.72 (s, 10H, C$_S$*H*$_S$, $\nu_{1/2}$ = 10 Hz). ^{31}P{^{1}H} NMR (121.5 MHz): δ −12.79 (s, $\nu_{1/2}$ = 51 Hz).

{[CpCo(P═O(OC$_2$D$_5$)$_2$)$_3$]$_2$Eu}$^+$ Cl$^-$, *d$_{60}$-**4a***. Complex *d*$_{60}$-**4a** was prepared using the same procedure as **3a** starting from *d*$_{30}$-**1a** and EuCl$_3$(H$_2$O)$_6$. Yield: 0.091 g (74%). Mp. 161−162 °C. IR (thin film, NaCl): 2226m, 2144w, 2103w, 1424w, 1187s, 1136s, 1088s, 1060s, 1010s, 829s, 732w, 693m, 674m cm^{-1}. ^{1}H NMR (CDCl$_3$, 300 MHz, 22 °C): δ 6.05 (s, ∼9 equiv H$_2$O, $\nu_{1/2}$ = 20 Hz), 0.73 (s, C$_S$*H*$_S$, $\nu_{1/2}$ = 7 Hz). ^{2}H NMR (CHCl$_3$, 55.3 MHz): δ 5.97 (s, 12D, C*D*$_A$D$_B$, $\nu_{1/2}$ = 5 Hz), 5.62 (s, 12D, CD$_A$*D*$_B$, $\nu_{1/2}$ = 5 Hz), 2.42 (s, 36D, C*D*$_3$, $\nu_{1/2}$ = 3 Hz). ^{31}P{^{1}H} NMR (121.5 MHz): δ −12.33 (s, $\nu_{1/2}$ = 65 Hz).

{[CpCo(P═O(OEt)$_2$)$_3$]$_2$Tb}$^+$ Cl$^-$, ***5a***. Complex **5a** was prepared as a yellow solid using the same procedure as **3a** starting from **1a** and TbCl$_3$(H$_2$O)$_6$. Yield: 0.19 g (73%). Mp. 145−147 °C. IR (thin film, NaCl): 2976m, 2927w, 2899w, 1386w, 1128s, 1042s, 935s, 834w, 770w, 729w cm^{-1}. ^{1}H NMR (CDCl$_3$, 300 MHz, 22 °C): δ 146.89 (s, 10H, C$_S$*H*$_S$, $\nu_{1/2}$ = 150 Hz), −40.47 (s, 36H, C*H*$_3$, $\nu_{1/2}$ = 124 Hz), −58.50 (s, 12H, C*H*$_A$H$_B$, $\nu_{1/2}$ = 418 Hz), −66.80 (s, 12H, CH$_A$*H*$_B$, $\nu_{1/2}$ = 410 Hz), −125.43 (s, ∼2 equiv H$_2$O, $\nu_{1/2}$ = 1527 Hz).

{[CpCo(P═O(OC$_2$D$_5$)$_2$)$_3$]$_2$Tb}$^+$ Cl$^-$, *d$_{60}$-**5a***. Complex *d*$_{60}$-**5a** was prepared using the same procedure as **3a** starting from *d*$_{30}$-**1a** and TbCl$_3$(H$_2$O)$_6$. Yield: 0.10 g (81%). Mp. 130−131 °C. IR (thin film, NaCl): 2225s, 2144m, 2102m, 1425w, 1186s, 1136s, 1089m, 1060m, 1008s, 928m, 829m, 731w, 692m, 673m cm^{-1}. ^{1}H NMR (CDCl$_3$, 300 MHz, 22 °C): δ 141.42 (s, C$_S$*H*$_S$, $\nu_{1/2}$ = 1800 Hz), −84.72 (s, ∼2 equiv H$_2$O, $\nu_{1/2}$ = 1354 Hz).

{[CpCo(P═O(OPh)$_2$)$_3$]$_2$Tb}$^+$ Cl$^-$, ***5b***. Complex **5b** was prepared as a yellow solid using the same procedure as **3b** starting from **1b** and TbCl$_3$(H$_2$O)$_6$. Yield: 0.083 g (85%). Mp. 281 °C (dec). IR (thin film, NaCl): 3039w, 1590s, 1488s 1207s, 1185m, 1163m, 1138s, 1111m, 1024w, 913s, 893s, 844w, 763m, 729m, 690m cm^{-1}. ^{1}H NMR (CDCl$_3$, 300 MHz, 22 °C): δ 180.44 (s, 10H, C$_S$*H*$_S$, $\nu_{1/2}$ = 841 Hz), −44.55 (s, 12H, *p*-aryl*H*, $\nu_{1/2}$ = 153 Hz), −62.60 (s, 24H, *o*/*m*-aryl*H*, $\nu_{1/2}$ = 242 Hz), −112.68 (s, 24H, *o*/*m*-aryl*H*, $\nu_{1/2}$ = 1174 Hz).

{[CpCo(P═O(OC$_6$D$_5$)$_2$)$_3$]$_2$Tb}$^+$ Cl$^-$, *d$_{60}$-**5b***. Complex *d*$_{60}$-**5b** was prepared using the same procedure as **3b** starting from *d*$_{30}$-**1b** and TbCl$_3$(H$_2$O)$_6$. Yield: 0.067 g (68%). Mp. 284 °C (dec). IR (thin film, NaCl): 2277w, 1557m, 1373s, 1155s, 1136s, 963w, 898s, 853m, 805s, 771w cm^{-1}. ^{1}H NMR (CDCl$_3$, 300 MHz, 22 °C): δ 174 (s, C$_S$*H*$_S$, $\nu_{1/2}$ = 2243 Hz).

{[CpCo(P═O(OEt)$_2$)$_3$]$_2$Yb}$^+$ Cl$^-$, ***6a***. Complex **6a** was prepared as a yellow solid using the same procedure as **3a** starting from **1a** and YbCl$_3$(H$_2$O)$_6$. Yield: 0.382 g (83%). Mp. 190−191 °C. IR (thin film, NaCl): 2977m, 2928w, 2899w, 1387w, 1110s, 1038s, 937s, 835w, 772w, 728w cm^{-1}. ^{1}H NMR (CDCl$_3$, 300 MHz, 22 °C): δ 9.81 (s, 24H, C*H*$_2$, $\nu_{1/2}$ = 42 Hz), 5.55 (s, 36H, C*H*$_3$, $\nu_{1/2}$ = 14 Hz), 4.06 (s, ∼2 equiv H$_2$O, $\nu_{1/2}$ = 18 Hz), −4.79 (s, 10H, C$_S$*H*$_S$, $\nu_{1/2}$ = 7 Hz). ^{31}P{^{1}H} NMR (121.5 MHz): δ 67.77 (s, $\nu_{1/2}$ = 76 Hz).

{[CpCo(P═O(OC$_2$D$_5$)$_2$)$_3$]$_2$Yb}$^+$ Cl$^-$, *d$_{60}$-**6a***. Complex *d*$_{60}$-**6a** was prepared using the same procedure as **3a** starting from *d*$_{30}$-**1a** and YbCl$_3$(H$_2$O)$_6$. Yield: 0.174 g (76%). Mp. 199−200 °C. IR (thin film, NaCl): 2226m, 2143w, 2116w, 1423w, 1187w, 1123s, 1086m, 1055m, 1006s, 986s, 824w, 694w, 675w cm^{-1}. ^{1}H NMR (CDCl$_3$, 300 MHz, 22 °C): δ 1.72 (s, ∼8 equiv H$_2$O, $\nu_{1/2}$ = 7 Hz), −4.81 (s, C$_S$*H*$_S$, $\nu_{1/2}$ = 7 Hz). ^{2}H (CHCl$_3$, 55.3 MHz): δ 9.79 (s, 12D, C*D*$_A$D$_B$, $\nu_{1/2}$ = 5 Hz), 9.68 (s, 12D, CD$_A$*D*$_B$, $\nu_{1/2}$ = 5 Hz), 5.56 (s, 36D, C*D*$_3$, $\nu_{1/2}$ = 4 Hz). ^{31}P{^{1}H} NMR (CDCl$_3$, 121.5 MHz): δ 67.89 (s, $\nu_{1/2}$ = 71 Hz).

{[CpCo(P═O(OPh)$_2$)$_3$]$_2$Yb}$^+$ Cl$^-$, ***6b***. Complex **6b** was prepared as a yellow solid using the same procedure as **3b** starting from **1b** and YbCl$_3$(H$_2$O)$_6$. Yield: 0.204 g (93%). Mp. 283 °C (dec). IR(thin film, NaCl): 3040w, 1590s, 1487s 1208s, 1185m, 1162m, 1081s, 1069m, 1024w, 913s, 888s, 847w, 770w, 757m, 689m cm^{-1}. ^{1}H NMR (CDCl$_3$, 300 MHz, 22 °C): δ 15.72 (s, 24H, *o*/*m*-aryl*H*, $\nu_{1/2}$ = 20 Hz), 11.44 (s, 24H, *o*/*m*-aryl*H*, $\nu_{1/2}$ = 20 Hz), 10.30 (s, 12H, *p*-aryl*H*, $\nu_{1/2}$ = 14 Hz), 1.40 (s, ∼9 equiv H$_2$O, $\nu_{1/2}$ = 9 Hz), −6.01 (s, 10H, C$_S$*H*$_S$, $\nu_{1/2}$ = 10 Hz). ^{31}P{^{1}H} NMR (CDCl$_3$, 121.5 MHz): δ 48.40 (s, $\nu_{1/2}$ = 51 Hz).

{[CpCo(P═O(OC$_6$D$_5$)$_2$)$_3$]$_2$Yb}$^+$ Cl$^-$, *d$_{60}$-**6b***. Complex *d*$_{60}$-**6b** was prepared using the same procedure as **3b** starting from *d*$_{30}$-**1b** and YbCl$_3$(H$_2$O)$_6$. Yield: 0.096 g (88%). Mp. 278 °C (dec). IR (thin film, NaCl): 2273w, 1556m, 1370s, 1155m, 1129m, 1080s, 960w, 905s, 856w, 807m, 770w cm^{-1}. ^{1}H NMR (CDCl$_3$, 300 MHz, 22 °C): δ −5.91 (s, C$_S$*H*$_S$, $\nu_{1/2}$ = 7 Hz), 1.48 (s, ∼9 equiv H$_2$O, $\nu_{1/2}$ = 10 Hz). ^{31}P{^{1}H} NMR (CDCl$_3$, 121.5 MHz): δ 47.68 (s, $\nu_{1/2}$ = 42 Hz).

{[CpCo(P═O(OPh)$_2$)$_3$]$_2$Yb}$^+$ {CoCl$_3$(THF)}$^-$·2 C$_6$H$_6$, ***7***. Complex **7** was isolated as a teal green crystalline solid in yields ranging from 10% to 65% in various trials as a byproduct in the synthesis of **6b** from **1b** and YbCl$_3$(H$_2$O)$_6$. Recrystallation of green **7** from acetone containing NaCl results in isolation of yellow **6b** in quantitative yield. Mp. 218−222 °C. IR (thin film, KBr): 2980w, 2929w, 1719w, 1590m, 1488s, 1454w, 1423w, 1204s, 1162m, 1081m, 1024m, 914s, 889s, 766m, 689m cm^{-1}. ^{1}H NMR (CDCl$_3$, 300 MHz, 22 °C): δ 12.49 (s, 24H, *o*/*m*-aryl*H*), 10.55 (s, 24H, *o*/*m*-aryl*H*), 9.62 (s, 12H, *p*-aryl*H*), −3.09 (s, 10H, C$_S$*H*$_S$). MS (+LSIMS): 1820.1 amu.

Kinetic Experiments. The following procedure describes the kinetic experiment for the *d*$_0$-**6a** and *d*$_{60}$-**6a** crossover experiment; all other kinetic runs were performed in an analogous fashion using the appropriate lanthanide, ligand, and solvent combination.

Solutions of **6a** and *d*$_{60}$-**6a** (10 mg of each) in HPLC-grade acetonitrile (10.00 mL) were prepared separately and then diluted 100-fold to give solutions with a final concentration of 10 μg/mL. A 0.500 mL aliquot of each solution was added to a vial and mixed for 10 s, and samples of this mixture were injected into the Q-TOF II mass spectrometer running in +ESI MS mode. Spectra were collected every 5 min for the first hour, followed by every 30 min for the next 6 h, and then every hour for the next 18 h. For other complexes, the sampling rate was adjusted as appropriate. In all cases, the reaction was followed until thermodynamic equilibrium (1:2:1 ratio of *d*$_0$/*d*$_{30}$/*d*$_{60}$ isotopomers) was established. The total counts for the major mass peaks of each isotopomer were used to establish the relative concentrations of each species. The mass spectrometer response was assumed to be identical for the different isotopomers of the complex in all cases. The effect of water content in the acetonitrile solvent on the exchange rate was examined for **5a** using solvent mixtures containing 0%, 10%, 20%, 30%, 40%, and 50% (v/v) water to acetonitrile. The maximum water content of 50% was dictated by the solubility limit of **5a** in the mixed solvent.

X-ray Crystallography. Crystals of compound **7** were grown from benzene. A suitable crystal was selected, attached to a glass fiber, and data were collected at 90(2) K using a Bruker/Siemens SMART APEX instrument (Mo Kα radiation, λ = 0.71073 Å) equipped with a Cryocool NeverIce low-temperature device. Data were measured using omega scans 0.3° per frame for 30 s, and a full sphere of data was collected. A total of 2400 frames were collected with a final resolution of 0.83 Å. Cell parameters were retrieved using *SMART*[21] software and refined using *SAINTPlus*[22] on all observed reflections. Data reduction and correction for Lp and decay were performed using the *SAINTPlus*[22] software. Absorption corrections were applied using SADABS.[23] The structure was solved by direct methods and refined by least-squares method on F^2 using the *SHELXTL*[24] program package. The structure was solved in the space group $P2_12_12_1$ (no. 19) by analysis of systematic absences. Various phenyl rings (C12, 61:39%; C53, 50%; C59, 66:34%), one Cp ring (C42, 54:46%) and solvents (C87, 70:30%; C93, 69:31%) were disordered. Disordered atoms were held isotropic and some restraints (distance and displacement) were applied. All other non-hydrogen atoms were refined anisotropically.

No decomposition was observed during data collection. Details of the data collection and refinement are given in Table 3. Further details are provided in the Supporting Information.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Tables of atomic coordinates, bond distances, and angles, and anisotropic thermal parameters for **7**; plots of $1/[d_{60}]$ vs time (**4a**, **5a** from 10% to 50% H_2O in ACN, **5b** and **6a** in ACN and 50% H_2O in ACN); TGA plots (**3a**, **5a**, **6b**); variable temperature ^1H NMR for **6b** and molecular ion isotope pattern/simulation comparisons for the cations of **3a**−**6a**. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: djberg@uvic.ca.

Present Addresses

[†]Nordion Inc., 4004 Westbrook Mall, Vancouver, BC, Canada V6T 2A3.

[‡]University Research Office, 109 Morrill Hall, University of Idaho, Moscow, ID, USA 83844−3010.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

D.J.B. (Discovery Grant) gratefully acknowledges the support of the Natural Sciences and Engineering Research Council of Canada.

■ REFERENCES

(1) Kläui, W. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 627.

(2) Kläui, W.; Kunz, P. C.; Seidel, S. N.; Gladysz, J. A. *Inorg. Synth.* **2010**, *35*, 125.

(3) (a) Aime, S.; Geninatti Crich, S.; Gianolio, E.; Giovenzana, G. B.; Tei, L.; Terreno, E. *Coord. Chem. Rev.* **2006**, *250*, 1562. (b) Strijkers, G. J.; Mulder, M.; Willem, J.; van Tilborg, F.; Geralda, A.; Nicolay, K. *Curr. Med. Chem. - Anti-cancer Agents* **2007**, *7*, 291.

(4) (a) Zhu, X.-J.; Wang, P.; Leung, H. W. C.; Wong, W.-K.; Wong, W.-Y.; Kwong, D. W. J. *Chem.—Eur. J.* **2011**, *17*, 7041. (b) Ke, H.; Wong, W.-K.; Wong, W.-Y.; Tam, H.-L.; Poon, C.-T.; Jiang, F. *Eur. J. Inorg. Chem.* **2009**, 1243. (c) Zhu, X.-J.; Jiang, F.-L.; Poon, C.-T.; Wong, W.-K.; Wong, W.-Y. *Eur. J. Inorg. Chem.* **2008**, 3151. (d) Jiang, F.-L.; Wong, W.-K.; Zhu, X.-J.; Zhou, G.-J.; Wong, W.-Y.; Wu, P.-L.; Tam, H.-L.; Cheah, K.-W.; Ye, C.; Liu, Y. *Eur. J. Inorg. Chem.* **2007**, 3365. (e) Zhu, X.-J.; Wong, W.-K.; Lo, W.-L.; Wong, W.-Y. *Chem. Commun.* **2005**, 1022. (f) He, H.; Wong, W.-K.; Guo, J.; Li, K.-F.; Wong, W.-Y.; Lo, W.-K.; Cheah, K.-W. *Inorg. Chim. Acta* **2004**, *357*, 4379. (g) Wong, W.-Y.; Li, K.-F.; Cheah, K.-W.; Xue, F.; Mak, T. C. W. *J. Chem. Soc., Dalton Trans.* **2001**, 3092.

(5) Sang, H. H.; Park, S.; Jeong, J. H. *Bull. Korean Chem. Soc.* **1999**, *20*, 741.

(6) Yi, X.-Y.; Sung, H. H. Y.; Williams, I. D.; Leung, W.-H. *Chem. Commun.* **2008**, 3269.

(7) (a) Roh, S.-G.; Jeong, J. H. *Acta Crystallogr., Sect. C* **2000**, *56*, 120. (b) Han, S.-H.; Roh, S.-G.; Jeong, J. H. *Polyhedron* **1999**, *18*, 3027.

(8) Kim, K.-C.; Park, Y.-C.; Jeong, J. H. *Bull. Korean Chem. Soc.* **1997**, *18*, 670.

(9) (a) Englert, U.; Ganter, B.; Wagner, T.; Kläui, W. Z. *Anorg. Allg. Chem.* **1998**, *624*, 970. (b) Cho, I. Y.; Yeo, H. J.; Jeong, J. H.; Song, C. E. *Acta Crystallogr., Sect. C* **1995**, *51*, 2035.

(10) Electrospray MS has been used to determine the rate of ligand exchange between platinum centers that form supramolecular polygons: Zheng, Y.-R.; Stang, P. J. *J. Am. Chem. Soc.* **2009**, *131*, 3487.

(11) (a) Kläui, W.; Neukomm, H.; Werner, H.; Huttner, G. *Chem. Ber.* **1977**, *110*, 2283. (b) Kläui, W. *Z. Naturforsch.* **1979**, *34B*, 1403.

(12) Li, L.; Stevens, E. D.; Nolan, S. P. *Organometallics* **1992**, *11*, 3452.

(13) Solari, E.; Corazza, F.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Chem. Soc., Dalton Trans.* **1990**, 1345.

(14) Farrugia, L. J. *J. Appl. Crystallogr.* **1997**, *30*, 565.

(15) Weinmann, H. J.; Mühler, A.; Radüchel, B. in *Biomedical Magnetic Resonance Imaging and Spectroscopy*, Young, I. R., Ed.; John Wiley and Sons Ltd.: Chichester, 2000; p 705.

(16) The response factor of the mass spectrometer to the d_0-, d_{30}-, and d_{60}-isotopomers is assumed to be identical in all cases. Starting concentrations were selected to ensure good signal-to-noise ratio without overloading the instrument.

(17) Shannon, R. D. *Acta Crystallogr.* **1976**, *32*, 751.

(18) (a) Kläui, W.; Scotti, M. D.; Valderamma, M.; Rojas, S.; Sheldrick, G. M.; Jones, P. G.; Schroeder, T. *Angew. Chem.* **1985**, *97*, 697. (b) Kläui, W.; Asbahr, H. O.; Schramm, G.; Englert, U. *Chem. Ber.* **1997**, *130*, 1223.

(19) King, R. B. *Inorg. Chem.* **1966**, *5*, 83.

(20) Ludewig, D.; Eiserbeck, W.; Feike, E. Z. *Chemie* **1984**, *24*, 290.

(21) *SMART* v 5.632; Bruker AXS Inc., Madison, WI, 2005.

(22) *SAINTPlus* v 7.23a; Data Reduction and Correction Program; Bruker AXS Inc., Madison, WI, 2004.

(23) *SADABS* v 2004−1; Empirical Absorption Correction Program; Bruker AXS Inc., Madison, WI, 2004.

(24) Sheldrick, G. M. *SHELXTL* v 6.14; Structure Determination Software Suite; Bruker AXS, Madison, WI, 2004.