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Assessing the Effects of Metal Ion Proximity on a *trans*-Ir(CO)Cl(phosphine)$_2$ Unit. Structural Studies of Potassium(I), Tin(II), and Lead(II) Complexes of (crown-P$_2$)Ir(CO)Cl

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Addition of lead(II) or tin(III) salts to (crown-P$_2$)Ir(CO)Cl (crown-P$_2$ is $Ph_2PCH_2N\{CH_2CH_2OCH_2CH_2OCH_2CH_2\}_2NCH_2PPh_2$) results in incorporation of the added main-group ion into the diaza crown ether portion. Yellow-orange crystals of [ClPb(crown-P$_2$)Ir(CO)Cl]Cl·2CH_2Cl_2 crystallize in the orthorhombic space group $Pc2_1b$ (No. 29) with a = 9.766 (4) Å, b = 22.291 (8) Å, and c = 23.159 (10) Å at 130 K with Z = 4. Refinement of 288 parameters and 3321 reflections yielded R = 0.070 and R_w = 0.074. The lead ion is coordinated to a terminal chloride and surrounded by the diaza-crown ligand so that it sits 3.117 (1) Å above the nearly planar *trans*-Ir(CO)ClP$_2$ portion. Yellow-orange needles of [ClSn(crown-P$_2$)Ir(CO)Cl]SnCl$_3$·CHCl$_3$ also form in the orthorhombic space group $Pc2_1b$ (No. 29) with a = 9.719 (2) Å, b = 22.391 (5) Å, and c = 22.782 (7) Å at 130 K with Z = 4. Refinement of 2876 reflection and 300 parameters gave R = 0.0569 and R_w = 0.059. The cation is similar to the lead analogue with the Sn–Ir distance of 2.920 (2) Å. Potassium iodide reacts with (crown-P$_2$)Ir(CO)Cl to form [K(crown-P$_2$)Ir(CO)I]I, which crystallizes as a tris(dichloromethane) solvate in the orthorhombic space group *Pbca* with a = 21.936 (2) Å, b = 21.868 (12) Å, and c = 21.511 (8) Å at 130 K with Z = 8. Refinement of 303 parameters and 2761 reflections yielded R = 0.059 and R_w = 0.056. The potassium sits within the diaza-crown portion, 3.331 (6) Å away from the iridium. The lead/iridium and tin/iridium complexes show distinctly new electronic absorption spectra indicative of Pb–Ir and Sn–Ir bonding. These complexes are photoluminescent at 77 K in frozen dichloromethane solution. In contrast, the potassium and sodium adducts of (crown-P$_2$)Ir(CO)Cl show only minor perturbations of the characteristic absorption spectrum of the Ir(CO)ClP$_2$ unit and do not show photoluminescence.

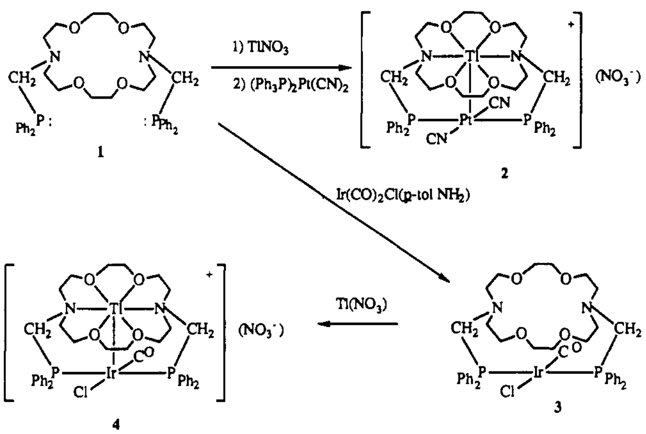
Introduction

The hybrid ligand crown-P$_2$ (**1**; scheme I) was initially prepared[1] in order to provide a ligand host that would stabilize the highly ionic Tl–Pt bond in $Tl_2Pt(CN)_4$.[2,3] This platinum complex has a pseudooctahedral structure with the one-coordinate thallium ions located 3.140 (1) Å above and below the $Pt(CN)_4$ plane.[3] Addition of thallium(I) nitrate and bis(triphenylphosphine)platinum(II) dicyanide to crown-P$_2$ yields [Tl(crown-P$_2$)Pt(CN)](NO$_3$) (**2**), which forms colorless crystals with blue photoluminescence similar to that seen in $Tl_2Pt(CN)_4$.[1] Thus, crown-P$_2$ provides a pair of trans phosphine ligands that are similar enough to cyanide ligands to preserve the electronic structure of the platinum(II) unit, while the crown unit provides an environment that effectively competes with solvation of the thallium ion and facilitates the Pt–Tl bonding. Another virtue of crown-P$_2$ lies in its ability to allow the construction of new, but related, substances in which other planar d^8 metal ions replace platinum(II). Thus, treatment of crown-P$_2$ with Ir(CO)$_2$Cl(*p*-toluidine) yields the host **3**, which incorporates a Vaska-like *trans*-IrP$_2$(CO)Cl unit.[4] Addition of thallium(I) nitrate to **3** gives **4** in which a Ir–Tl unit is created.[4] The Tl–Ir bond length in **4** is 2.875 (1) Å. The electronic spectrum of **4** shows an intense band at 400 nm (ϵ = 19 700 M^{-1} cm^{-1}), which is clearly different from the absorption spectrum of **3**. Moreover, **4** shows intense photoluminescence (λ_{max} = 580 nm) at 77 K in frozen dichloromethane.

Here we explore the ability of **3** to provide a host for the coordination of other main-group ions. Two classes of these have been explored. Previous work on the binding of d^8 transition metal units to heavy main-group ions has indicated that the necessary electronic features for the main-group ion are filled s orbital (the 6s orbital in Tl(I)) and an empty p orbital.[5] Other ions that are isoelectronic with Tl(I), including Sn(II) and Pb(II), should also be capable of interaction with the iridium in **3** in a similar fashion. On the other hand, cations in group 1 lack a suitably high-energy filled s orbital. Thus, their interaction, if any, with **3** was anticipated to have different consequences.

While complex **3** provides a novel environment for examining the interaction between main-group ions and iridium centers, it is not the only complex so constructed. The metallomacrocycles **5**[6–9] and **7**[10] (Scheme II) are also capable of binding main-group metal ions, as shown in eqs 1 and 2. Consequently, it is instructive to compare **3** with **5** and **7** in terms of their abilities to interact with various metal ions.

Scheme I



Scheme II

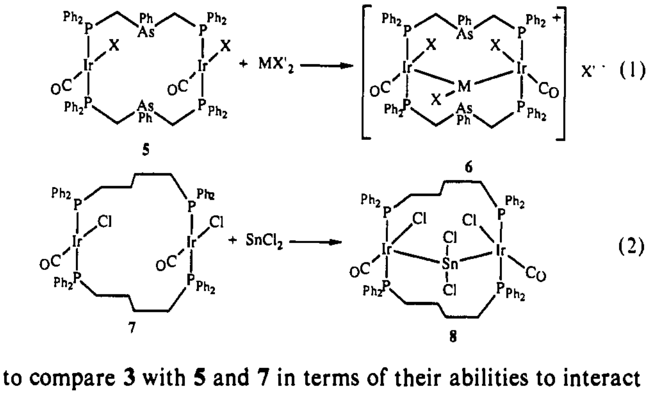


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Table I. Infrared and ^{31}P NMR Data

compd	IR: ν(CO), cm^{-1} [a]	$^{31}P\{^1H\}$ NMR: δ, ppm [b]
(crown-P_2)Ir(CO)Cl	1957	10.6
[ClSn(crown-P_2)Ir(CO)Cl]($SnCl_3$)	1974	25.3
[CH_3CO_2Pb(crown-P_2)Ir(CO)Cl](CH_3CO_2)	1974	22.7
[ClPb(crown-P_2)Ir(CO)Cl]Cl	1977	22.9
[ClPb(crown-P_2)Ir(CO)Cl](BPh_4)	1979, 1969 1986 [d]	23.0 [c]
[Pb(crown-P_2)Ir(CO)Cl](BPh_4)$_2$	2013	23.7 [c]
[Na(crown-P_2)Ir(CO)Cl](BPh_4)	1964	19.0
[Na(crown-P_2)Ir(CO)Br]Br	1963	17.6
[Na(crown-P_2)Ir(CO)I]I	1961	15.7
[K(crown-P_2)Ir(CO)Cl]PF_6	1970	15.7
[K(crown-P_2)Ir(CO)I]I	1969	11.4

[a] In Nujol mull. [b] In chloroform-*d* solution. [c] In acetonitrile-d_3 solution. [d] In dichloromethane solution.

Results

Synthetic Studies. The results of the insertion of a variety of ions into the diaza-crown portion of **3** are summarized in Scheme III. Complexes with Sn(II), Pb(II), K(I), and Na(I) bonded within the diaza-crown unit have been prepared and isolated. Addition of tin(II) chloride gives [ClSn(crown-P_2)Ir(CO)Cl]($SnCl_3$) (**9**). The addition of lead(II) acetate is accompanied by complications due to exchange of additional ligands on the lead. Reaction with lead(II) acetate alone gives (CH_3CO_2)Pb(crown-P_2)Ir(CO)Cl](CH_3CO_2) (**11**), whereas addition of lead(II) acetate and sodium tetraphenylborate yields [Pb(crown-P_2)Ir(CO)Cl](BPh_4)$_2$ (**10**). The infrared spectrum of **10** shows no evidence for bands of any acetate ion, while **11** shows bands at 1630 (m br) and 1565 cm^{-1} (m) that are absent in **10** and assigned to in the acetate ions. The ^1H NMR spectrum of the acetate complex **11** shows a resonance at 2.20 ppm, which is absent in the spectra of **10** and **12**. Addition of tetraphenylarsonium chloride to **10** yields [ClPb(crown-P_2)Ir(CO)Cl][BPh_4] (**12**). The acetate-containing complex [(CH_3CO_2)Pb(crown-P_2)Ir(CO)Cl](CH_3CO_2) (**11**) is unstable in chlorinated solvents. Treatment of **11** with sodium tetraphenylborate in dichloromethane also yields **12**, with the chloride ion coming from the solvent or solvent impurities. Attempts to grow X-ray diffraction quality crystals of the acetate complex **11** from dichloromethane produced the chloro complex [ClPb(crown-P_2)Ir(CO)Cl]Cl.

Addition of solution sodium halides in methanol to dichloromethane solutions of **3** results in incorporation of the sodium ion into the diaza crown and substitution of the chloride ligand on iridium when bromide or iodide salts are used. These sodium complexes have very limited stability in chlorinated solvents and their soluntions show signs of decomposition to unidentified products within a few hours. Addition of potassium iodide to **3** yields [K(crown-P_2)Ir(CO)I]I, while potassium hexafluorophosphate forms [K(crown-P_2)Ir(CO)Cl][PF_6]. These potassium complexes have considerably greater stability in chlorinated solvents than do their sodium analogues. Under similar conditions attempts to react rubidium tetraphenylborate or rubidium nitrate with **3** lead only to the recovery of unreacted **3**. Thus, this complex does not appear capable of binding rubidium. This is noteworthy since the ionic radii of Rb(I) and Tl(I) are similar (1.50 Å) and **3** does bind Tl(I).

The $^{31}P\{^1H\}$ NMR and infrared spectral data for these adducts are set out in Table I. Unique ^{31}P chemical shifts are seen for each species. This clearly indicates that each retains its integrity in solution. The infrared spectra in general show ν(CO) in the range characteristic of iridium(I) complexes.[11,12]

Table II. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($Å^2 \times 10^3$) for [ClPb(crown-P_2)Ir(CO)Cl]Cl·2CH_2Cl_2

	x	*y*	*z*	*U* [a]
Ir	1243 (1)	5000	5518 (1)	24 (1)*
Pb	2397 (1)	4180 (1)	4542 (1)	29 (1)*
Cl(1)	−677 (7)	4653 (3)	4984 (4)	33 (2)*
Cl(2)	3969 (12)	3635 (6)	3772 (5)	82 (5)*
Cl(3)	5039 (16)	2181 (5)	1769 (5)	54 (4)*
Cl(4)	4230 (14)	1289 (5)	2616 (6)	54 (5)*
Cl(5)	3929 (18)	2551 (6)	2879 (5)	55 (5)*
Cl(6)	348 (14)	997 (5)	2889 (5)	89 (5)*
Cl(7)	98 (20)	2214 (5)	3256 (7)	100 (10)*
Cl(8)	−2235 (18)	1589 (13)	2743 (11)	99 (14)*
Cl(9)	682 (20)	2184 (5)	1569 (5)	115 (7)*
P(1)	754 (8)	4215 (4)	6149 (3)	29 (2)*
P(2)	1137 (7)	5852 (3)	4934 (3)	28 (2)*
O(1)	442 (20)	3373 (10)	4178 (10)	41 (7)*
O(2)	935 (23)	4377 (9)	3546 (9)	44 (7)*
O(3)	4719 (23)	4815 (9)	4644 (9)	41 (7)*
O(4)	4401 (20)	3729 (10)	5280 (10)	39 (7)*
O(5)	3913 (21)	5305 (10)	6075 (9)	40 (7)*
N(1)	1559 (27)	3256 (10)	5360 (9)	30 (8)*
N(2)	2476 (28)	5328 (10)	3998 (11)	38 (9)*
C(13)	638 (32)	3470 (14)	5800 (14)	36 (7)
C(14)	917 (36)	2779 (15)	5013 (16)	45 (8)
C(15)	−135 (34)	3011 (14)	4628 (13)	38 (8)
C(16)	−648 (32)	3617 (14)	3779 (14)	36 (8)
C(17)	217 (37)	3895 (16)	3318 (16)	49 (9)
C(18)	1170 (30)	4846 (11)	3160 (13)	29 (7)
C(19)	2640 (39)	5238 (19)	3393 (18)	62 (11)
C(20)	3715 (34)	5622 (15)	4109 (16)	46 (9)
C(21)	5024 (32)	5175 (12)	4186 (13)	34 (7)
C(22)	5920 (34)	4439 (16)	4790 (15)	43 (8)
C(23)	5620 (44)	4136 (23)	5358 (18)	72 (12)
C(24)	3845 (33)	3503 (14)	5790 (14)	38 (7)
C(25)	2798 (32)	3036 (14)	5650 (14)	36 (7)
C(26)	1377 (30)	5690 (13)	4171 (13)	31 (7)
C(39)	2898 (23)	5193 (14)	5853 (14)	41 (8)

[a] Asterisk indicates equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor. Parameters for phenyl groups omitted; see supplementary material.

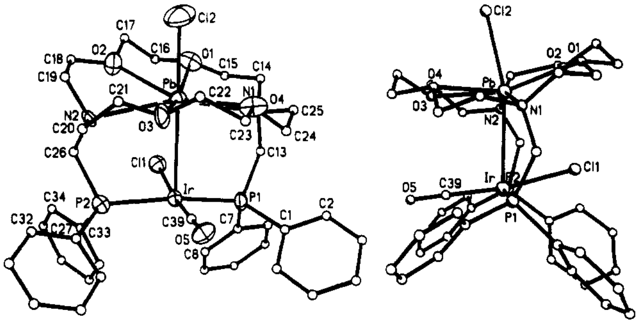

Figure 1. Two perspective views on the cation in [ClPb(crown-P_2)Ir(CO)Cl]Cl·2CH_2Cl_2. The one on the left shows the numbering system used for all crown-P_2 complexes considered here.

Structures of [ClPb(crown-P_2)Ir(CO)Cl]Cl·CH_2Cl_2 and [ClSn(crown-P_2)Ir(CO)Cl]($SnCl_3$)·$CHCl_3$. The lead/iridium complex crystallizes with one cation, a chloride, and two disordered molecules of dichloromethane in the asymmetric unit. Selected atomic coordinates are given in Table II. Two views of the cation are shown in Figure 1. Selected interatomic distances and angles are set out in Table III.

The complex cation consists of a planar iridium coordinated by the usual array of trans phosphine ligands, a terminal carbon monoxide, and a chloride ion. The distances and angles with the

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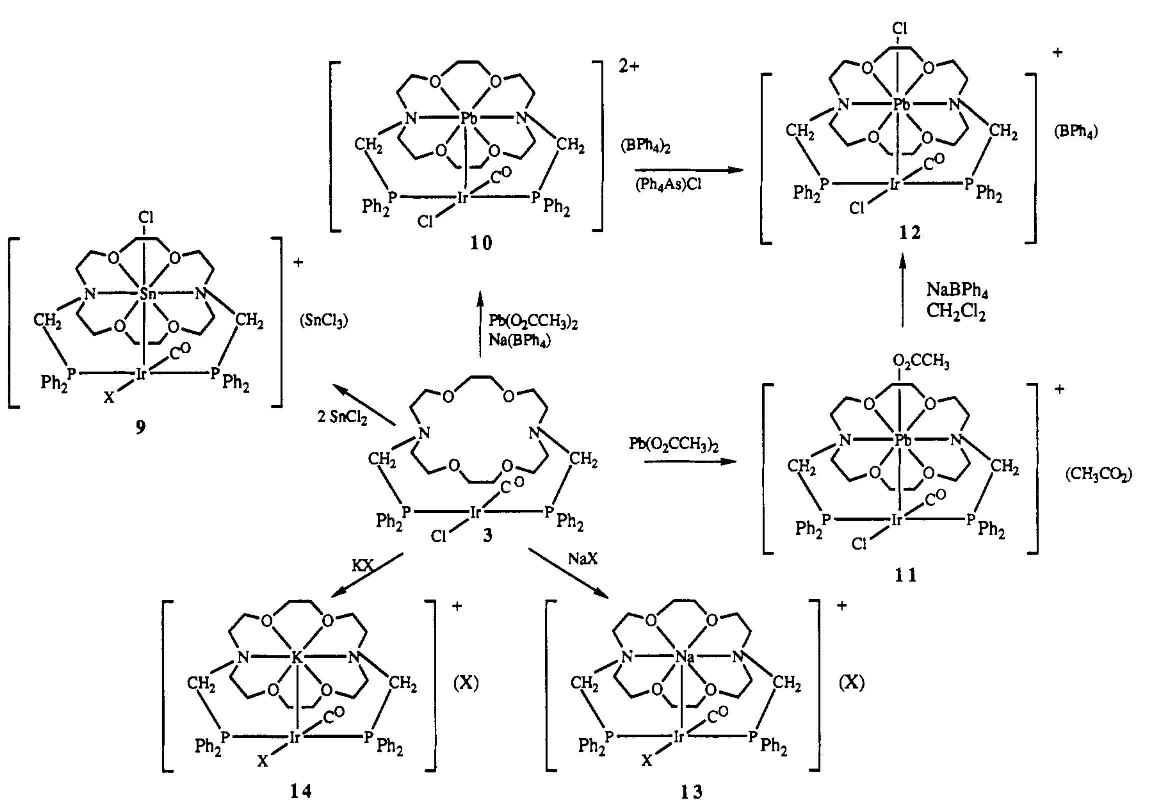
Scheme III



$IrP_2(CO)Cl$ unit are consistent with the parameters seen for other complexes of this type.[4,7-12]

The lead ion is located within the diaza-crown portion directly above the iridium center. A chloride ion is axially coordinated to the lead ion as well. The lead is asymmetrically positioned within the macrocycle so that it is closer to O(3) than the other oxygen atoms and closer to N(2) than N(1). The Pb–O distances are comparable to Pb–O distances observed in other macrocyclic complexes of lead.[13,14] However, the Pb–N distances (2.92 (2), 2.85 (2) Å) are longer than the range (2.41–2.75 Å) of Pb–N distances seen in other macrocycles.[13,16] The most relevant comparison can be made with (diaza-18-crown-6)Pb(SCN)$_2$, in which the lead resides in the same diaza-crown environment.[13] In this complex the Pb–N distance is 2.751 (6) Å, while the Pb–O distances are 2.787 (4) and 2.879 (5) Å.[13] Thus, the crown-P_2 environment in [ClPb(crown-P_2)Ir(CO)Cl]$^+$, because of the constraints of binding two metal ions, has caused alteration in the Pb–N distances. These constraints have produced an even more noticeable angular change. In (diaza-18-crown-6)Pb(SCN)$_2$ the two nitrogen and four oxygen donors form a nearly planar belt of donors that encircle the lead ion. In [ClPb(crown-P_2)Ir(CO)Cl]$^+$, however, that unit is not planar. The nitrogen atoms are pulled from the crown unit toward the methylene bridges.

The Pb–Ir distance is 3.117 (1) Å, which is 0.242 Å longer than the Tl–Ir distance seen in [Tl(crown-P_2)Ir(CO)Cl]$^+$.[4] This Pb–Ir distance is also considerably longer than the Pb–Ir distances (2.855 (2), 2.831 (2) Å) in the Ir–Pb–Ir chain in **6** (MX′ = PbI, X = I).[9] These are the only other Pb–Ir distances available for comparison.

The tin/iridium complex [ClSn(crown-P_2)Ir(CO)Cl]SnCl$_3$·CH$_2$Cl$_2$ is isostructural with the lead/iridium complex. The two cations occupy similar positions within the unit cell, while the spaces between these large cations are occupied by rather different entities in the two salts (a chloride ion and two disordered dichloromethane molecules for the lead complex; a SnCl$_3^-$ ion and two dichloromethane molecules in the tin case). Selected positional parameters are given in Table IV. Structural parameters for the tin/iridium complex are given in Table III. The major differences between the tin/iridium and lead/iridium complexes involve the shortening of the M–Ir and M–Cl bonds in the tin complexes. The tin ion is asymmetrically placed within the diaza-crown portion of the cation, and the degree of asymmetry is even more pronounced than it is in the lead/iridium complex.

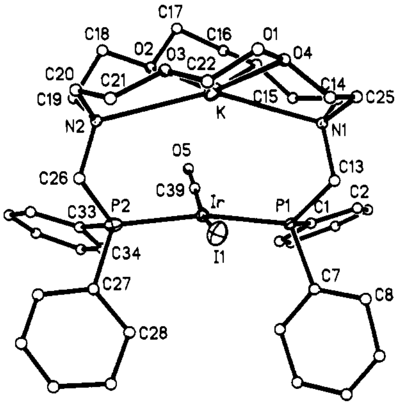


Figure 2. Perspective view of the cation in [K(crown-P_2)Ir(CO)I]I·3CH$_2$Cl$_2$.

The Sn–Ir distance (2.920 (2) Å) is longer than the Sn–Ir distances in the Ir–Sn–Ir chains in **6** (MX′ = SnCl, X = Cl) (2.741 (2), 2.742 (2) Å)[8] or in **8** (2.751 (1) Å).[10] It is also considerably longer than the Ir–Sn distances (2.57–2.64 Å) in complexes where the tin is part of a SnCl$_3^-$ ligand.[17,18] The Sn–Cl distance (2.528 (7) Å) is longer than the SnCl distances in **6** (MX′ = SnCl, X = Cl) (2.433 (7) Å) or **8** (2.459 (9) Å) and longer than the Sn–Cl distances (2.440 (11), 2.452 (13), 2.508 (9) Å) in the SnCl$_3^-$,

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Table III. Selected Interatomic Distances (Å) and Angles (deg) in $[ClM(crown\text{-}P_2)Ir(CO)Cl]^+$ (M = Sn, Pb) and in $[K(crown\text{-}P_2)Ir(CO)I]^+$

	M = Pb	M = Sn	K
Distances Involving Ir			
Ir–M	3.117 (1)	2.920 (2)	3.331 (6)
Ir–P(1)	2.331 (8)	2.291 (7)	2.319 (7)
Ir–P(2)	2.334 (8)	2.363 (6)	2.316 (7)
Ir–Cl	2.375 (7)	2.384 (6)	2.657 (3)[a]
Ir–C(39)	1.84 (2)	1.85 (2)	1.85 (2)
C(39)–O(5)	1.14 (3)	1.09 (3)	1.03 (3)
Distances Involving M			
M–N(1)	2.92 (2)	2.979 (1)	2.91 (2)
M–N(2)	2.85 (2)	2.793 (1)	2.99 (2)
M–O(1)	2.76 (2)	2.802 (1)	2.71 (2)
M–O(2)	2.75 (2)	2.722 (1)	2.74 (2)
M–O(3)	2.68 (2)	2.592 (1)	2.67 (2)
M–O(4)	2.79 (2)	2.797 (1)	2.70 (2)
M–Cl	2.648 (12)	2.528 (7)	
Angles Involving Ir			
M–Ir–P(1)	95.1 (2)	99.7 (2)	93.1 (2)
M–Ir–P(2)	94.2 (2)	94.0 (1)	97.0 (2)
M–Ir–Cl(1)	73.6 (2)	78.0 (10)	76.9 (1)[a]
M–Ir–C(39)	97.2 (9)	102.1 (6)	89.0 (8)
P(1)–Ir–P(2)	165.0 (3)	161.8 (2)	168.4 (2)
P(1)–Ir–Cl(1)	85.4 (3)	86.0 (2)	87.8 (2)[a]
P(1)–Ir–C(39)	95.2 (10)	96.2 (7)	92.9 (9)
P(2)–Ir–Cl(1)	85.9 (3) 88.8 (2)	85.2 (2)	88.8 (2)[a]
P(2)–Ir–C(39)	95.4 (10)	92.6 (7)	93.0 (9)
Cl(1)–Ir–C(39)	170.0 (10)	177.8 (7)	165.9 (8)
Angles Involving M			
Ir–M–Cl(2)	165.2 (3)	168.8 (2)	
Ir–M–N(1)	80.9 (4)	86.0 (3)	77.0 (4)
Ir–M–N(2)	78.7 (5)	83.7 (3)	73.5 (4)
Ir–M–O(1)	110.8 (4)	110.5 (3)	92.1 (4)
Ir–M–O(2)	109.1 (4)	110.2 (3)	87.2 (4)
Ir–M–O(3)	86.1 (5)	90.6 (3)	113.7 (5)
Ir–M–O(4)	91.2 (5)	92.4 (3)	121.5 (5)
N(1)–M–O(1)	62.8 (7)	60.6 (9)	62.5 (6)
N(1)–M–O(4)	62.9 (7)	62.2 (9)	65.5 (6)
N(2)–M–O(2)	60.0 (7)	60.4 (9)	
N(2)–M–O(3)	62.8 (7)	64.3 (9)	62.3 (6)
O(1)–M–O(2)	59.2 (6)	59.2 (9)	62.2 (5)
O(3)–M–O(4)	62.8 (6)	62.7 (9)	63.7 (6)
N(1)–M–N(2)		161.9 (10)	150.1 (6)
Cl(2)–M–N(1)	106.0 (5)	100.1 (8)	
Cl(2)–M–N(2)	95.7 (6)	97.4 (8)	
Cl(2)–M–O(1)	84.0 (5)	78.7 (7)	
Cl(2)–M–O(2)	79.0 (5)	79.7 (7)	
Cl(2)–M–O(3)	79.1 (5)	79.9 (7)	
Cl(2)–M–O(4)	80.8 (5)	78.0 (7)	
Angles Involving the Methylene Bridge			
P(1)–C(13)–N(1)	125 (2)	122 (2)	119 (2)
P(2)–C(26)–N(2)	119 (2)	117 (2)	115 (2)

[a] Iodide rather than chloride.

Table IV. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3) for $[ClSn(crown\text{-}P_2)Ir(CO)Cl]SnCl_3\cdot CHCl_3$

	x	*y*	*z*	*U*(eq)[a]
Ir	1314 (1)	5000	5483 (1)	18 (1)
Sn(1)	2457 (2)	4303 (1)	4515 (1)	24 (1)
Cl(1)	−708 (6)	4689 (3)	4974 (3)	26 (2)
Cl(2)	3888 (7)	3729 (3)	3780 (3)	41 (2)
P(1)	834 (6)	4245 (3)	6129 (3)	26 (2)
P(2)	1121 (6)	5883 (3)	4921 (2)	22 (1)
O(1)	593 (17)	3421 (8)	4157 (7)	30 (4)
O(2)	905 (19)	4452 (8)	3531 (8)	41 (5)
O(3)	4741 (14)	4897 (6)	4576 (6)	22 (4)
O(4)	4544 (16)	3834 (7)	5224 (7)	28 (4)
N(1)	1720 (21)	3322 (9)	5341 (9)	28 (5)
N(2)	2479 (19)	5401 (9)	3933 (8)	25 (5)
C(13)	751 (27)	3500 (12)	5779 (11)	34 (6)
C(14)	1170 (28)	2848 (12)	5012 (12)	37 (7)
C(15)	57 (33)	3004 (13)	4602 (12)	44 (7)
C(16)	−420 (29)	3623 (13)	3726 (11)	43 (7)
C(17)	335 (27)	3952 (11)	3254 (11)	32 (6)
C(18)	1107 (25)	4948 (14)	3144 (10)	37 (6)
C(19)	2341 (29)	5274 (13)	3310 (11)	40 (7)
C(20)	3761 (25)	5705 (12)	4068 (11)	34 (6)
C(21)	4992 (29)	5262 (11)	4089 (11)	36 (6)
C(22)	6005 (25)	4573 (11)	4753 (11)	30 (6)
C(23)	5671 (24)	4236 (11)	5302 (10)	26 (6)
C(24)	4050 (24)	3615 (10)	5754 (10)	25 (6)
C(25)	3008 (30)	3096 (13)	5617 (13)	43 (7)
C(26)	1326 (27)	5773 (13)	4122 (11)	38 (6)
C(39)	2884 (19)	5268 (10)	5859 (9)	25 (6)
O(5)	3861 (18)	5370 (8)	6074 (7)	37 (4)
Sn(2)	1151 (4)	1893 (1)	7526 (1)	95 (1)
Cl(3)	−420 (12)	2206 (3)	6708 (3)	66 (3)
Cl(4)	−540 (13)	1179 (4)	7890 (3)	81 (4)
Cl(5)	2265 (13)	1121 (6)	6928 (5)	105 (5)
Cl(6)	4497 (13)	2229 (4)	1820 (3)	86 (4)
Cl(7)	3568 (11)	2549 (3)	2983 (3)	71 (4)
Cl(8)	4587 (10)	1361 (3)	2758 (4)	69 (3)
C(40)	3794 (26)	1993 (8)	2482 (7)	57 (8)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor. Parameters for phenyl groups omitted; see supplementary material.

which is the counterion in the present structure.

Structure of $[K(crown\text{-}P_2)Ir(CO)I]I\cdot 3CH_2Cl_2$. The asymmetric unit consists of the complex cation, an iodide ion, and three dichloromethane molecules. Selected atomic coordinates are given in Table V. A view of the cation is shown in Figure 2. Selected interatomic distances and angles are given in Table III.

The structure of the cation resembles those of the lead/iridium and tin/iridium cations that were described in the previous section. However, there is no additional ligand besides the diaza-crown portion that is coordinated to the potassium ion. Also, an iodide ligand rather than a chloride ligand is attached to the iridium.

The environment of the potassium ion can best be compared to the potassium coordination in [(diaza-18-crown-6)K]SCN.[19] In this complex the potassium resides within the center of an N_2O_4 array of donors, which are very nearly coplanar. In contrast in $[K(crown\text{-}P_2)Ir(CO)I]^+$, the diaza-crown portion is saddle shaped and the nitrogen atoms are drawn downward by the methylene bridges. The K–N distance (2.856 (3) Å) in [(diaza-18-crown-6)K]$^+$ is shorter than the K–N distances (2.91 (2), 2.99 (2) Å) in the potassium/iridium complex, while the reverse is true for the K–O distances. The K–O distances in [(diaza-18-crown-6)K]$^+$ (2.836 (3), 2.825 (3) Å) are longer than the K–O distances (2.67 (2)–2.74 (2) Å) in the potassium/iridium complex.

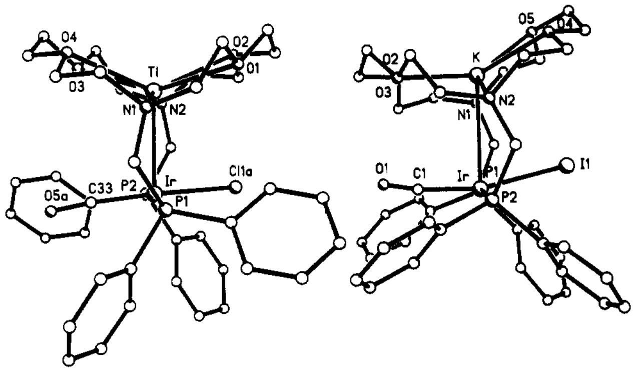

Figure 3. Views from similar vantage points that compare the structures of $[Tl(crown\text{-}P_2)Ir(CO)Cl]^+$ (left) and $[K(crown\text{-}P_2)Ir(CO)I]^+$ (right). The line between K and Ir on the right emphasizes their separation but does not represent a chemical bond.

The K–Ir distance (3.331 (6) Å) is the longest of the M–Ir distances found within the group of complexes derived from **3**. This potassium/iridium complex was made specifically for comparison with the thallium/iridium complex **4**.[4] Both contain a

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[19] Moras, D.; Metz, B.; Herceg, M.; Weiss, R. *Bull. Soc. Chim. Fr.* **1972**, 551.

Table V. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$) for [K(crown-P_2)Ir(CO)I]I·3CH_2Cl_2

	x	y	z	U(eq)[a]
Ir	954 (1)	2187 (1)	500 (1)	11 (1)
I(1)	1684 (1)	2863 (1)	−206 (1)	28 (1)
I(2)	1103 (1)	7528 (1)	2341 (1)	31 (1)
K	1756 (3)	1147 (3)	−281 (3)	18 (2)
P(1)	1677 (3)	2263 (3)	1283 (3)	13 (2)
P(2)	191 (3)	2316 (3)	−232 (3)	15 (3)
O(1)	1723 (8)	353 (8)	685 (8)	21 (5)
O(2)	764 (8)	395 (8)	−184 (8)	21 (5)
O(3)	2001 (9)	1468 (9)	−1450 (9)	31 (5)
O(4)	2941 (9)	1326 (9)	−563 (10)	36 (5)
O(5)	335 (7)	1167 (8)	1051 (7)	10 (4)
N(1)	2531 (10)	1411 (10)	784 (9)	14 (5)
N(2)	668 (10)	1438 (10)	−1063 (10)	16 (6)
C(1)	1484 (11)	1946 (10)	2046 (10)	20 (6)
C(2)	1918 (13)	1731 (12)	2473 (13)	25 (8)
C(3)	1738 (14)	1509 (13)	3050 (12)	25 (8)
C(4)	1137 (13)	1510 (12)	3199 (13)	26 (8)
C(5)	675 (13)	1741 (12)	2792 (12)	18 (7)
C(6)	873 (12)	1955 (11)	2230 (11)	17 (7)
C(7)	1824 (13)	3075 (12)	1471 (12)	18 (7)
C(8)	2369 (13)	3286 (13)	1690 (12)	19 (7)
C(9)	2381 (14)	3926 (14)	1868 (13)	29 (8)
C(10)	1906 (13)	4277 (14)	1863 (12)	25 (8)
C(11)	1361 (15)	4053 (14)	1687 (14)	38 (9)
C(12)	1295 (13)	3435 (12)	1483 (12)	23 (8)
C(13)	2449 (11)	2015 (12)	1084 (12)	21 (8)
C(14)	2499 (13)	891 (13)	1238 (13)	29 (8)
C(15)	1844 (13)	621 (13)	1268 (13)	28 (8)
C(16)	1219 (12)	−56 (11)	708 (11)	16 (7)
C(17)	1006 (13)	−161 (11)	42 (11)	19 (7)
C(18)	546 (13)	353 (12)	−819 (12)	21 (8)
C(19)	232 (12)	939 (12)	−973 (13)	25 (8)
C(20)	948 (13)	1413 (11)	−1709 (11)	16 (6)
C(21)	1523 (13)	1766 (13)	−1789 (13)	26 (8)
C(22)	2562 (14)	1823 (15)	−1456 (15)	45 (10)
C(23)	3033 (14)	1516 (15)	−1195 (14)	38 (9)
C(24)	3194 (13)	1687 (12)	−100 (12)	24 (8)
C(25)	3169 (12)	1419 (12)	515 (13)	22 (7)
C(26)	378 (12)	2055 (12)	−1030 (11)	23 (7)
C(27)	34 (11)	3125 (11)	−409 (11)	11 (7)
C(28)	254 (12)	3604 (13)	−40 (13)	24 (8)
C(29)	140 (14)	4228 (14)	−234 (15)	39 (9)
C(30)	−231 (15)	4302 (16)	−769 (15)	45 (10)
C(31)	−412 (14)	3840 (15)	−1107 (15)	41 (9)
C(32)	−325 (12)	3249 (12)	−945 (11)	14 (7)
C(33)	−563 (11)	2043 (11)	−1 (10)	10 (6)
C(34)	−735 (12)	2089 (13)	606 (12)	29 (8)
C(35)	−1309 (11)	1867 (11)	830 (12)	12 (7)
C(36)	−1706 (13)	1656 (12)	393 (12)	22 (8)
C(37)	−1580 (13)	1637 (12)	−223 (13)	24 (7)
C(38)	−993 (12)	1845 (10)	−427 (11)	15 (6)
C(39)	546 (15)	1560 (15)	896 (14)	36 (9)
Cl(1)	370 (5)	5341 (4)	2637 (4)	51 (4)
Cl(2)	1614 (4)	5656 (5)	2951 (5)	60 (4)
Cl(3)	1097 (5)	9764 (5)	2787 (5)	82 (5)
Cl(4)	390 (5)	9046 (5)	3671 (5)	73 (5)
Cl(5)	1718 (5)	370 (4)	5244 (5)	65 (4)
Cl(6)	2376 (5)	217 (5)	4084 (5)	63 (4)
C(40)	871 (16)	5868 (16)	2977 (16)	59 (12)
C(41)	645 (16)	9103 (15)	2883 (15)	48 (11)
C(42)	1680 (14)	139 (15)	4445 (15)	49 (10)

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

monocation that is held within a common environment. The 0.456-Å difference between the K–Ir distance and the Tl–Ir distance causes changes within the crown-P_2 ligand. These are best seen by examining Figure 3, which shows the two complexes from similar vantage points. As Figure 3 shows, the potassium-/iridium complexes has a structure similar to that of the lead/iridium and tin/iridium complexes. Both bridging methylene groups that connect the phosphine portion to the diaza-crown part lie on the same side of the K–Ir axis and to the side of the Ir–I bond. As a consequence, O(4) and O(5) are further from the coordination plane of the iridium than are O(2) and O(3). In contrast, in [Tl(crown-P_2)Ir(CO)Cl]$^+$ the methylene groups are arranged on opposite sides of the Tl–Ir axis and all four oxygen atoms of the diazacrown portion are roughly equidistant from the coordination plane of iridium.

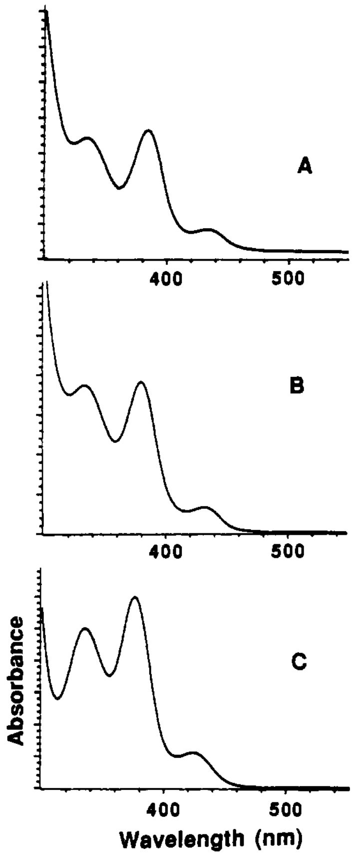

Figure 4. Electronic absorption spectra of dichloromethane solutions at 23 °C of (A) (crown-P_2)Ir(CO)Cl, (B) [Na(crown-P_2)Ir(CO)Cl][BPh_4], and (C) [K(crown-P_2)Ir(CO)Cl]PF_6.

Electronic Absorption and Emission Spectra. Relevant absorption and emission data are presented in Table VI. Figure 4 compares the electronic spectrum of (crown-P_2)Ir(CO)Cl with those of [Na(crown-P_2)Ir(CO)Cl]BPh_4 and [K(crown-P_2)Ir(CO)Cl]PF_6. The spectra are similar and show the typical three-band pattern that is characteristic of Vaska-type iridium(I) complexes.[20] Only modest shifts in the energies of these transitions occur when a cation is bound to the diaza crown ether portion. Consequently, the effect of the electric field of the cation on the iridium chromophore is slight.

In contrast, binding ions with electronic configurations that supply a filled s and an empty p orbital produces major perturbations of the electronic spectra. Relevant data are shown in Figure 5. The top trace, A, shows the absorption spectrum of [ClSn(crown-P_2)Ir(CO)Cl]$^+$, while the lower trace, C, shows the absorption spectrum of [(CH_3CO_2)Pb(crown-P_2)Ir(CO)Cl]$^+$. In both cases an intense transition near 400 nm is seen than has $\epsilon \sim 20000$. Additionally a weaker feature, taken to be the spin-forbidden counterpart of this spin-allowed bond, is seen at lower energies (ca. 505–450 nm). Similar spectroscopic features have also been seen for [Tl(crown-P_2)Ir(CO)Cl]$^+$ (see Table VI).[4] Both [ClSn(crown-P_2)Ir(CO)Cl]$^+$ and [(CH_3CO_2)Pb(crown-P_2)Ir(CO)Cl]$^+$ are photoluminescent. Emission spectra taken in frozen dichloromethane solution at 77 K are shown in traces B and D of Figure 5. The excitation spectra for both complexes parallel to their absorption spectra. Solution of these tin/iridium and lead/iridium complexes do not show photoluminesce at 23 °C.

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(20) Brady, R.; Flynn, B. R.; Geoffrey, G. L.; Gray, H. B.; Peone, J., Jr.; Vaska, L. *Inorg. Chem.* **1976**, *15*, 1485.

Table VI. Electronic Absorption and Emission Data

compd	absorption:[a] λ_{max}, nm (ϵ, M^{-1} cm^{-1})	emission:[b] λ_{max}, nm
$Ir(PPh_3)_2(CO)Cl$	439 (730), 387 (4040), 339 (3160)[c]	*e*
(crown-P_2)Ir(CO)Cl	434, 384, 334[d]	none obsd
$Ir(PPh_3)_2(CO)Br$	443 (800), 390 (3960), 343 (3100)[c]	*e*
$Ir(PPh_3)_2(CO)I$	451 (590), 397 (2570), 356 (2100)[c]	*e*
[Na(crown-P_2)Ir(CO)Cl](BPh_4)	431 (440), 380 (2300), 335 (2100)	none obsd
[Na(crown-P_2)Ir(CO)Br]Br	436 (480), 383 (2200), 341 (1900)	none obsd
[Na(crown-P_2)Ir(CO)I]I	442 (610), 390 (2100), 346 (2000)	none obsd
[K(crown-P_2)Ir(CO)Cl][PF_6]	426 (500), 376 (2840), 336 (2340)	none obsd
[K(crown-P_2)Ir(CO)I]I	431 (690), 386 (2230), 345 (2300)	none obsd
[ClSn(crown-P_2)Ir(CO)Cl]($SnCl_3$)	504 (310), 422 (23 800)	621
[CH_3CO_2Pb(crown-P_2)Ir(CO)Cl](CH_3CO_2)	456 (560), 394 (15 200)	500
[ClPb(crown-P_2)Ir(CO)Cl]Cl	470 (650), 394 (19 700), 310 (6050)	*e*
[ClPb(crown-P_2)Ir(CO)Cl](BPh_4)	470 (260), 396 (21 700), 310 (5000)	506
[Pb(crown-P_2)Ir(CO)Cl]$(BPh_4)_2$	476 (770), 376 (17 300)	498
[Tl(crown-P_2)Ir(CO)Cl] (No. 3)	500 (452), 400 (19 700)[f]	580[f]

[a] Dichloromethane solutions at 23 °C. [b] Frozen dichloromethane solutions at 77 K. [c] In benzene solution; data from ref 20. [d] Instability in solution precluded accurate evaluation of ϵ; values are presumably similar to those of $Ir(PPh_3)_2(CO)Cl$. [e] Not examined. [f] Data from ref 4.

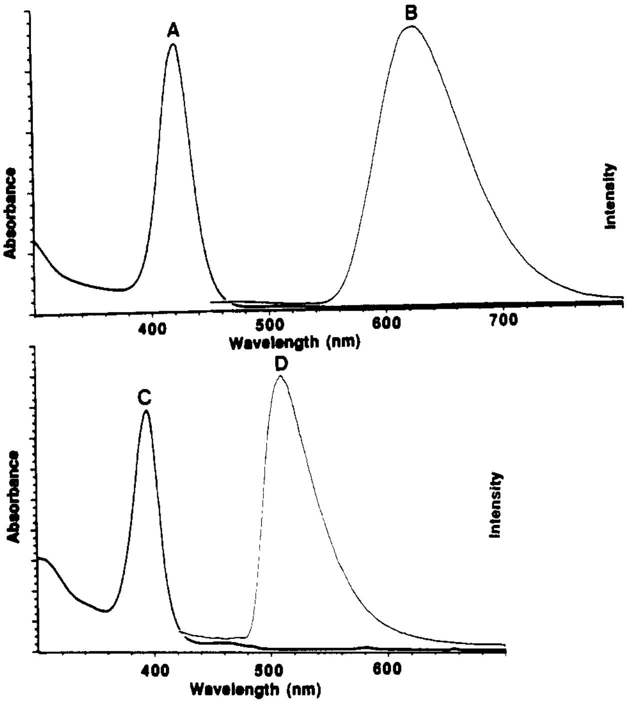

Figure 5. Top: (A) Absorption spectrum in dichloromethane at 23 °C and (B) uncorrected emission spectrum from frozen dichloromethane solution at 77 K of [ClSn(crown-P_2)Ir(CO)Cl]($SnCl_3$). Bottom: (C) Absorption spectrum in dichloromethane at 23 °C and (D) uncorrected emission spectrum from a frozen dichloromethane solution at 77 K of [(CH_3CO_2)Pb(crown-P_2)Ir(CO)Cl](CH_3CO_2).

No photoluminescence was observed for (crown-P_2)Ir(CO)Cl itself or for the sodium and potassium complexes under similar conditions (either in solution at 23 °C or in frozen solution at 77 K).

Discussion

The results described here and in past studies[4] show that (crown-P_2)Ir(CO)Cl is capable of binding a variety of metal ions within the diaza-crown portion. Only those main-group ions with an s^2 electronic configuration (Tl(I), Sn(II), Pb(II)) are able to perturb the electronic structure of the *trans*-Ir(CO)ClP_2 unit. Binding of K(I) or Na(I) in roughly the same site has only a minor effect upon the electronic structure of the iridium, as measured by changes in the absorption spectrum.

Within those main-group ions that do bind to iridium the M–Ir distances increase in the order Tl–Ir (2.875 (1) Å) < Sn–Ir (2.920 (2) Å) < Pb–Ir (3.117 (1) Å). This order does not follow the trend in the ionic radii of these ions (which is Sn(II) (1.18 Å) ~ Pb(II) (1.19 Å) < Tl(I) (1.50 Å)).[21] Nor does it follow the trend in covalent radii: Sn (1.40 Å) < Pb (1.46 Å) ~ Tl (1.47 Å). The order of M–Ir distances in Ir–M–Ir units within the metallomacrocycles **6** is also different (Sn–Ir (2.741 (2), 2.742 (2) Å) < Pb–Ir (2.855 (2), 2.831 (2) Å) < Tl–Ir (2.958 (1), 2.979 (1) Å). The M–Ir distances in the (crown-P_2)Ir(CO)Cl complexes must reflect competing effects of bonding of M to the aza-crown portion and to the iridium center. With tin(II) and lead(II) the presence of an additional chloride ligand that is nearly colinear with the Sn–Ir and Pb–Ir bonds may serve to lengthen these bonds. Notice, however, that the potassium complex, which shows no spectroscopic perturbation of the Ir(CO)ClP_2 chromophore, has the longest M–Ir separation (3.331 (6) Å) within the group of crystallographically characterized complexes. It is interesting that rubidium(I), which has the same ionic radius of thallium(I), does not bind to **3**. We take this to be a further indication of the difference between the alkali-metal cations and the main-group cations with the s^2 electronic configuration.

The bonding of the main-group ions—Pb(II), Sn(II), and Tl(I)—to iridium in these complexes can be considered in light of the theoretical work[2] on $Tl_2Pt(CN)_4$ with the proviso that only one metal–metal bond is present. In $Tl_2Pt(CN)_4$ the Tl–Pt bonds are largely electrostatic with a small covalent component.[2] That covalent component comes from interaction of the filled $5d_{z^2}$ orbital of platinum, the filled 6s orbital of thallium, and the empty p_z orbitals on both (with *z* the Tl–Pt–Tl axis). In the main group/iridium complexes described here similar interactions between the iridium filled $5d_{z^2}$, the main-group filled 5- or 6s orbital, and the empty p_z orbitals on each metal are responsible for the covalent bond, which may make up a large share of the bonding, since the Ir(CO)ClP_2 unit is uncharged. As noted earlier for the thallium/iridium complex **4**,[4] the intense absorption seen near 400 nm for the tin/iridium and the lead/iridium complexes may be the counterpart of the $\sigma^* \rightarrow \sigma$ transition seen for d^8–d^8 face-to-face platinum metal dimers. However, accurate spectroscopic assignments must await further study, since relativistic effects play an important role in determining the excited-state energies. On the basis of the large Stokes shift and the inability to observe the luminescence at temperatures above 77 K, the photoemission is assigned tentatively as phosphorescence.

Experimental Section

Preparation of Compounds. All preparations were performed on a Schlenk line under a purified dinitrogen atmosphere. Solvents were dried by standard techniques. Crown-P_2[1] and (crown-P_2)Ir(CO)Cl[4] were prepared as previously described. To avoid oxidation of the iridium complex **3**, fresh samples were prepared just before use.

[ClSn(crown-P_2)Ir(CO)Cl]$SnCl_3$·$CHCl_3$ (9). Solid tin(II) chloride dihydrate (100 mg, 0.45 mmol) was added to a solution of 100 mg (0.109 mmol) of (crown-P_2)Ir(CO)Cl in 3 mL of chloroform. The yellow solution immediately became deep green and then after 1–2 min turned deep orange. The solution was filtered to remove unreacted tin(II) chloride, and diethyl ether was added to the orange filtrate. The dark yellow precipitate was collected by filtration and recrystallized from

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(21) Shannon, R. D. *Acta. Crystallogr.* **1976**, *A32*, 751.

Table VII. Crystal Data, Data Collection, and Structure Solution Parameters

	[ClSn(crown-P_2)Ir(CO)Cl]($SnCl_3$)·$CHCl_3$	[ClPb(crown-P_2)Ir(CO)Cl]Cl·$2CH_2Cl_2$	[K(crown-P_2)Ir(CO)I]I·$3CH_2Cl_2$
formula	$C_{40}H_{49}Cl_8IrN_2O_5P_2Sn_2$	$C_{41}H_{52}Cl_7IrN_2O_5P_2Pb$	$C_{42}H_{54}Cl_6I_2IrKN_2O_5P_2$
fw	1412.9	1362.42	1426.6
space group	*Pb*2$_1$*b* (*bca* of No. 29)	*Pc*2$_1$*b* (No. 29)	*Pbca* (No. 61)
a, Å	9.719 (2)	9.766 (4)	21.936 (12)
b, Å	22.391 (5)	22.291 (8)	21.868 (12)
c, Å	22.782 (7)	23.159 (10)	21.511 (8)
V, Å^3	4958 (2)	5042 (4)	10319 (9)
T, deg	130 K	130 K	130 K
Z	4	4	8
d_{calcd}, g cm^{-3}	1.893	1.79	1.837
μ(Mo Kα), cm^{-1}	42.1	34.9	42.6
range of transm factors	0.56–0.81	0.22–0.38	0.28–0.49
2θ range, deg	0–45.0	0–50	0–50
R^a	0.057	0.070	0.059
$R_w{}^a$	0.059 [$w = \sigma^2(F_o) + 0.001F_o)^{-1}$]	0.074 [$w = 1/\sigma^2(F_o)$]	0.056 [$w = (\sigma^2(F_o) + 0.0006F_o)^{-1}$]

^{a} $R = \sum|F_o| - |F_c|/|F_o|$ and $R_w = \sum|F_o| - |F_c|w^{1/2}/\sum|F_o w^{1/2}]$.

chloroform/ethyl ether to give orange crystals of the product; yield 80 mg, 52%.

[Pb(crown-P_2)Ir(CO)Cl](BPh_4)$_2$ (10). A solution of 58 mg (0.15 mmol) of lead(II) acetate trihydrate in 2 mL of methanol was added to a stirred solution of (crown-P_2)Ir(Cl)Cl in 5 mL of dichloromethane. The yellow solution brightened in hue after 30 min of stirring. A 6-fold excess of sodium tetraphenylborate (314 mg, 0.918 mmol) in 4 mL of methanol was added, and the mixture was stirred for an additional 30 min. Addition of 9 mL of methanol caused a pale yellow solid to precipitate. This was collected by filtration, washed with methanol and ethyl ether, and dried in vacuum; yield 195 mg, 73%. Anal. Calcd for $C_{87}H_{88}B_2ClIrN_2O_5P_2Pb$: C, 59.37; H, 5.04; N, 1.59. Found: C, 59.78; H, 4.99; N, 1.54.

[(CH_3CO_2)Pb(crown-P_2)Ir(CO)Cl](CH_3CO_2) (11). A solution of 58 mg (0.15 mmol) of lead(II) acetate trihydrate in 3 mL of methanol was added to a solution of (crown-P_2)Ir(CO)Cl in 10 mL of dichloromethane. After being stirred for 30 min, the pale yellow solution was concentrated to half its volume. Addition of ethyl ether gave a bright yellow precipitate, which was collected by filtration, washed with diethyl ether, and vacuum dried; yield 93 mg, 49%. Anal. Calcd for $C_{43}H_{54}ClIrN_2O_9P_2Pb$: C, 41.66; H, 4.39; N, 2.26. Found: C, 38.45; H, 4.58, N, 2.07.

[ClPb(crown-P_2)Ir(CO)Cl](BPh_4) (12). Method 1. Solid tetraphenylarsonium chloride (13 mg, 0.031 mmol) was added to a stirred solution of 50 mg (0.028 mmol) of [Pb(crown-P_2)Ir(CO)Cl](BPh_4)$_2$ in 8 mL of dichloromethane. Immediately the solution acquired a greenish yellow color. After the solution was stirred for 45 min, 15 mL of methanol was added. A white solid formed and was removed by filtration. The yellow filtrate was concentrated under reduced pressure. The yellow solid that formed was collected by filtration, washed with methanol and ethyl ether, and vacuum dried; yield 15 mg, 36%. Anal. Calcd for $C_{63}H_{68}BCl_2IrN_2O_5P_2Pb$: C, 51.26; H, 4.64; N, 1.90. Found: C, 52.01; H, 4.64; N, 1.67.

Method 2. A 6-fold excess of sodium tetraphenylborate (41 mg, 0.12 mmol) in 1 mL of methanol was added to a yellow solution of [CH_3CO_2Pb(crown-P_2)Ir(CO)Cl](CH_3CO_2) in 3 mL of dichloromethane. Immediately the color changed from yellow to greenish yellow. After 1 h of stirring, 5 mL of methanol were added dropwise to the solution. The yellow product was collected by filtration and recrystallized from acetonitrile; yield 18 mg, 61%.

[Na(crown-P_2)Ir(CO)Cl][BPh_4]. A solution of sodium tetraphenylborate (53 mg, 0.153 mmol) in 1.5 mL of methanol was added to a solution of 100 mg (0.109 mmol) of (crown-P_2)Ir(CO)Cl in 5 mL of dichloromethane. After the solution had stirred for 1 h, it was evaporated to dryness. The solid residue was dissolved in dichloromethane, and the solution was filtered to remove unreacted sodium tetraphenylborate. The yellow filtrate was concentrated, and ethyl ether was added slowly to give the product as a pale yellow solid (yield 70 mg, 51%). Anal. Calcd for $C_{63}H_{68}BClIrN_2NaO_5P_2$: C, 60.22; H, 5.45; N, 2.23. Found: C, 61.00; H, 4.40; N, 2.44.

[Na(crown-P_2)Ir(CO)Br]Br·CH_2Cl_2 (13) (X = Br). A 5-fold excess of sodium bromide dissolved in 3 mL of methanol was added to a solution of 100 mg (0.109 mmol) of (crown-P_2)Ir(CO)Cl in 10 mL of dichloromethane. The cloudy solution was stirred for 1 h. After removal of the solvents by rotary evaporation, the residue was dissolved in dichloromethane and the mixture filtered to remove the excess sodium bromide. Dropwise addition of ethyl ether to the solution resulted in the precipitation of the yellow, crystalline product, which was collected by filtration, washed with ethyl ether, and vacuum dried; yield 61 mg, 53%. Anal. Calcd for $C_{40}H_{50}Br_2Cl_2IrN_2NaO_5P_2$: C, 41.89; H, 4.39; N, 2.44. Found: C, 41.77; H, 3.94; N, 2.58.

[Na(crown-P_2)Ir(CO)I]I (13) (X = I). Bright yellow microcrystals were obtained from the reaction described by [Na(crown-P_2)Ir(CO)-Br]Br with sodium iodide in place of sodium bromide; yield 82 mg, 65%. Anal. Calcd for $C_{39}H_{48}I_2IrN_2NaO_5P_2$: C, 40.53; H, 4.19; N, 2.42. Found: C, 39.41; H, 3.95; N, 2.51.

[K(crown-P_2)Ir(CO)Cl](PF_6)·0.5CH_2Cl_2 (14). Yellow microcrystals were obtained from potassium hexafluorophosphate by using the procedure described for [Na(crown-P_2)Ir(COBr]Br; yield 92 mg, 65%. Anal. Calcd for $C_{39}H_{48}ClF_6KIrN_2O_5P_3$·0.5$CH_2Cl_2$: C, 41.58; H, 4.33; N, 2.46. Found: C, 41.35; H, 4.25; N, 2.34.

[K(crown-P_2)Ir(CO)I]I. Yellow microcrystals were obtained by the route described for [Na(crown-P_2)Ir(CO)Br]Br with potassium iodide instead of sodium bromide; yield 73%. Anal. Calcd for $C_{39}H_{48}KI_2IrN_2O_5P_2$: C, 39.97; H, 4.13, N, 2.39. Found: C, 39.48; H, 4.09; N, 2.51.

Physical Measurements. Infrared spectra were obtained from mineral oil (Nujol) mulls between KBr plates on an IBM IR32 spectrophotometer. Solution infrared spectra were measured from cells equipped with CaF_2 windows. The ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded on a General Electric QE-300 NMR spectrometer at 300.15 (^1H) and 121.7 (^{31}P) MHz. Chemical shifts were referenced internally to tetramethylsilane (^1H) and externally to 85% H_3PO_4 (^{31}P), following the high-field positive convention. Electronic spectra were recorded with a Hewlett-Packard 8450A spectrometer. Uncorrected emission spectra were obtained by using a Perkin-Elmer MHF-44B fluorescence spectrometer.

X-ray Data Collection. [ClPb(crown-P_2)Ir(CO)Cl]Cl·2CH_2Cl_2. Yellow-orange needles of the compound were obtained by diffusion of ethyl ether into a dichloromethane solution of [(CH_3CO_2)Pb(crown-P_2)Ir-(CO)Cl](CH_3CO_2). The chloride ions were derived from the solvent as described above. The crystals were coated with a light hydrocarbon oil to prevent cracking upon drying. A well-formed needle was mounted on a glass fiber with silicon grease and placed in the nitrogen stream at 130 K from the modified LT-1 low-temperature apparatus affixed to a Syntex P2$_1$ diffractometer. Only random fluctuations of less than 2% in the intensities of two standard reflections were observed during the course of data collection. Conditions for present reflections of 0*kl*, *l* = 2*n*, *hk*0, *k* = 2*n*, and *h*00, no conditions, indicated the two possible space groups of *Pcmb* (No. 57) and *Pc*2$_1$*b* (No. 29). The data were corrected for Lorentz and polarization effects. Crystal data are given in Table VII.

[ClSn(crown-P_2)Ir(CO)Cl]($SnCl_3$)·$CHCl_3$. Orange-yellow plates were obtained by diffusion of ethyl ether into a chloroform solution of the complex. These were handled as described above and mounted in the cold stream of a Siemens R3m/V diffractometer. The complex is isostructural with the lead/iridium analogue.

[K(crown-P_2)Ir(CO)I]I·3CH_2Cl_2. Yellow prisms were obtained by diffusion of ethyl ether into a dichloromethane solution of the complex. The crystals were handled as described above.

Solution and Refinement of Structures. [ClPb(crown-P_2)Ir(CO)Cl]-Cl·2CH_2Cl_2. Conditions for present reflections of 0*kl*, *l* = 2*n*, *hk*0, *k* = 2*n*, and *h*00, no conditions, indicated the two possible space groups of *Pcmb* (No. 57) and *Pc*2$_1$*b* (No. 29). The structure was solved by Patterson and difference Fourier methods in the space group Pc2$_1$*b*. Unreasonable high symmetry precluded solution of the structure in *Pcmb*. Computer programs are from SHELXTL, Version 5, installed on a Data General Eclipse computer. Neutral-atom scattering factors and corrections for anomalous dispersion were taken from a standard source.[22] The handedness of the structure was determined by a SHELXTL routine in which a variable of either 1 or −1 refines all $\Delta f''$ values. Disorder in the two dichloromethane molecules was modeled by assigning 70, 70, and 60% weights to three chlorines of one molecule and 100, 60, and 40% weights to the three chlorines of the other. The carbons of these two molecules were not included in the structure factor calculation, although they did appear as small peaks in the final difference map. The carbon of the carbonyl group was reset during refinement to a distance of 1.85 (2) Å from the iridium. Phenyl rings were refined as rigid hexagons with C–C distances of 1.395 Å. Hydrogen atoms were included at calculated positions by using a riding model and C–H distances of 0.96 Å. The thermal parameters for the hydrogen atoms were fixed at 1.2 times the thermal parameter of the bonded carbon. Two low angle reflections, 020 and 002, were omitted from the data set, since they appeared to suffer from extinction. An absorption correction was applied.[23] Final refinement was carried out with anisotropic thermal parameters for the Ir, Pb, Cl, P, N, and O atoms. The largest peak in a final difference map had a value of 1.7 e Å^{-3}, located 0.93 Å from Pb.

[ClSn(crown-P_2)Ir(CO)Cl]$SnCl_3$·$CHCl_3$. The structure was refined by direct methods with the Siemens SHELXTL PLUS (VMS) programs. No constraints were applied to the phenyl carbons; however, the Ir–C distance was reset to 1.85 (2) Å with each cycle of refinement Neutral-atom scattering factors and corrections for anomalous dispersion were taken from a standard source. Hydrogen atoms were included at calculated positions by using a riding model and C–H distances of 0.96 Å. The thermal parameters for the hydrogen atoms were fixed at a *U* of 0.04 Å^2. The handedness was determined as above. An absorption correction was applied. Final refinement was carried out with anisotropic thermal parameters for the Ir, Sn, Cl, and P atoms. The largest peak in a final difference map had a value of 3.0 e Å^{-3}, 1.2 Å from Sn(2).

[K(crown-P_2)Ir(CO)I]I·3CH_2Cl_2. Determination of the space group followed from the observed conditions $0kl$, $k = 2n$, $h0l$, $l = 2n$, and $hk0$, $h = 2n$. The structure was solved by direct methods with the Siemens SHELXTL PLUS (VMS) programs. Hydrogen atoms were included at calculated positions by using a riding model and C–H distances of 0.96 Å. The thermal parameters for the hydrogen atoms were fixed at a U = 0.03 Å^2 except for those of the dichloromethanes, which were fixed at 0.06 Å^2. An absorption correction was applied. Final refinement was carried out with anisotropic thermal parameters for the Ir, K, Cl, P, and I atoms. The largest peak in a final difference map had a value of 1.2 e Å^{-3}, 1.3 Å from I(2).

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Registry No. **9**·$CHCl_3$, 135107-48-1; **10**, 135107-50-5; **11**, 135107-52-7; **12**·Cl, 135107-47-0; **12**·Cl·2CH_2Cl_2, 135107-63-0; **12**·BPh_4, 135107-54-9; **13** (X = Br), 135107-57-2; **13** (X = I), 135107-58-3; **14**, 135107-60-7; (crown-P_2)Ir(CO)Cl, 132673-23-5; [Na(crown-P_2)Ir(CO)Cl][BPh_4], 135107-56-1; [K(crown-P_2)Ir(CO)I]I, 135107-61-8; [K(crown-P_2)Ir(CO)I]I·3CH_2Cl_2, 135107-64-1.

Supplementary Material Available: Tables of atomic coordinates, bond distances, bond angles, anisotropic thermal parameters, hydrogen atom positions, and crystal refinement data for [ClPb(crown-P_2)Ir(CO)Cl]Cl·2CH_2Cl_2, [ClSn(crown-P_2)Ir(CO)Cl]($SnCl_3$)·$CHCl_3$, and [K(crown-P_2)Ir(CO)I]I·3CH_2Cl_2 (21 pages); listings of observed and calculated structure factors (63 pages). Ordering information is given on any current masthead page.

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Preparation of 1,1,5,5-Tetraphenyl-3,7-diaryl-1,5-diphosphatetrazocines and 1,1,3,3,5-Pentaphenyldiphosphatriazine and the X-ray Structure of 1,5-$Ph_4P_2N_4C_2(C_6H_4CH_3\text{-}4)_2$

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The reactions of Li[PhC($NSiMe_3$)$_2$] or $ArCN_2(SiMe_3)_3$ (Ar = $C_6H_4CH_3$-4, $C_6H_4CF_3$-4) with Ph_2PCl_3 produce 1,5-$Ph_4P_2N_4C_2Ar_2$ (Ar = C_6H_5 (**4a**), 4-$CH_3C_6H_4$ (**4c**)) and, as a minor product, the six-membered ring $Ph_4P_2N_3CPh$ (**1b**). Compound **1b** is also obtained from the reaction of PhC[N($SiMe_3$)$_2$]($NPPh_2$) with 2 molar equiv of benzeneselenenyl chloride in CH_2Cl_2. Compounds **1b** and **4a–c** exhibit high thermal stability with no indication of polymer formation below 250 °C. An X-ray structural determination of **4b** showed that it consists of an eight-membered ring in a distorted boat–boat conformation with the phosphorus atoms out of and on the same side of the plane and the carbon atoms on the other side of the plane. One of the nitrogen atoms also deviates significantly from the best plane. The crystals of **4b** are monoclinic, space group $P2_1/c$, with a = 17.236 (3) Å, b = 19.558 (1) Å, c = 20.694 (3) Å, β = 107.66 (1)°, V = 6647 (2) Å^3, and Z = 8. Two crystallographically independent molecules of **4b** are present in the asymmetric unit. The final R and R_w values were 0.059 and 0.039, respectively. The average P–N and C–N bond lengths are ca. 1.60 and 1.31 Å, respectively, and the endocyclic bond angles at phosphorus are ca. 126°. There are two distinct bond angles at nitrogen for both molecules with values of ca. 127 and 139°.

Introduction

Phosphorus–nitrogen heterocycles that contain a third heteroelement (heterocyclophosphazenes) are of interest from the viewpoint of structure and bonding[1] and as precursors for inorganic polymers with unusual properties.[2] Several examples of the hybrid inorganic ring systems P_2N_3C (diphosphatriazines) (**1**)[3] and PN_3C_2 (phosphatriazines) (**2**)[4] are known, and very recently the first examples of poly(carbophosphazenes) have been obtained via thermolysis of **1a**.[2c] Two derivatives of the eight-membered 1,3- and 1,5-$P_2N_4C_2$ rings (diphosphatetrazocines), **3** and **4** (R = Ph,

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