$C\mathit{H}_2C(CH_3)_3$), 3.74 (sept, 4 H, $C\mathit{H}(CH_3)_2$), 6.96 (m, 6 H, aryl).

Bis((2,6-diisopropylphenyl)imido)dimesitylmolybdenum(VI) (3). To 300 mg of 1 (0.51 mmol) in diethyl ether was added 1.30 g of a 1 M solution of MesMgBr in THF (Aldrich, 1.30 mmol), and the mixture was stirred for 48 h. Filtration and evaporation gave a burgandy red solid, which was recrystallized with loss from pentane at -40 °C. Yield: 30%. Anal. Calcd for $MoC_{42}H_{56}N_2$: C, 73.68; H, 8.19; N, 4.09. Found: C, 73.53; H, 8.47; N, 4.05. IR (cm^{-1}): 1595 m, 1320 m, 1280 s, 1268 s, 1105 m, 979 s, 850 s, 798 s, 750 s, 585 w, 383 w, 350 w. ^{1}H NMR (ppm, C_6D_6): 0.96 (d, 24 H, $CH(C\mathit{H})_3)_2$), 2.08 (s, 6 H, *p*-CH_3(mesityl)), 2.88 (s, 12 H, *o*-CH_3(mesityl)), 3.90 (sept, 4 H, $C\mathit{H}(CH_3)_2$), 6.79 (s, 4 H, mesityl aryl), 6.96 (s, 6 H, aryl).

Bis((2,6-diisopropylphenyl)imido)bromomesitylmolybdenum(VI) (4). To 300 mg of the dichloro derivative 1 (0.52 mmol) in diethyl ether was added 650 mg of a 1 M solution of MesMgBr in THF (0.65 mmol), and the mixture was stirred for 12 h. Filtration and evaporation gave a bright red solid, which was recrystallized with loss from pentane at -40 °C. Yield: 25%. Anal. Calcd for $MoC_{33}H_{45}N_2Br$: C, 61.40; H, 7.03; N, 4.34. Found: C, 61.85; H, 7.41; N, 4.26. IR (cm^{-1}): 1600 m, 1370 m, 1330 w, 1290 w, 1280 m, 1265 m, 988 m, 975 m, 860 s, 808 s, 770 s, 765 s, 385 m, 365 m. ^{1}H NMR (ppm, C_6D_6): 1.08 (d, 24 H, $CH(C\mathit{H}_3)_2$), 2.00 (s, 3 H, *p*-CH_3(mesityl)), 2.75 (s, 6 H, *o*-CH_3(mesityl)), 3.82 (sept, 4 H, $C\mathit{H}(CH_3)_2$), 6.66 (s, 2 H, mesityl aryl), 6.97 (s, 6 H, aryl). The mass spectrum, although not showing the molecular ion peak, clearly exhibits a fragmentation pattern indicating the presence of bromide and not chloride.

Bis((2,6-diisopropylphenyl)imido)chloro(diethylamido)molybdenum(VI) (5) and Bis((2,6-diisopropylphenyl)imido)bis(diethylamido)molybdenum(VI) (6). A 1.50-g amount of dichloro derivative 1 (2.55 mmol) and 426 mg of lithium diethylamide (Aldrich, 5.39 mmol) were stirred in ether for 12 h. Filtration of liberated LiCl and evaporation gave a deep red oil, which was redissolved in pentane and cooled to -40 °C. The supernatant was decanted, leaving 50 mg (yield 5%) of a deep red solid of 5. Anal. Calcd for $MoC_{28}H_{44}N_3Cl$: C, 60.70; H, 7.95; N, 7.58. Found: C, 59.25; H, 7.85; N, 7.17. IR (cm^{-1}): 3040 w, 1575 w, 1410 s, 1350 m, 1315 s br, 1265 s br, 1240 m, 995 s, 970 m, 968 s, 928 m, 890 s, 788 s, 740 s br, 600 m, 582 m, 510 w, 420 w, 365 w. ^{1}H NMR (ppm, C_6D_6): 1.05 (t, 6 H, $N(CH_2C\mathit{H}_3)_2$), 1.23 (d, 24 H, $CH(C\mathit{H}_3)_2$), 3.27 (br q, 4 H, $N(C\mathit{H}_2CH_3)_2$), 4.07 (sept, 4 H, $C\mathit{H}(CH_3)_2$), 6.90-7.03 (m, 6 H, aryl).

Evaporation of the supernatant gave the bis(diethylamido) complex 6 as a deep red oil. Yield: 85%. Anal. Calcd for $MoC_{32}H_{54}N_4$: C, 64.86; H, 9.12. Found: C, 64.59; H, 9.26. IR (cm^{-1}): 3060 w, 1570 w, 1420 s, 1320 s br, 1265 s br, 1005 s, 973 m, 885 s, 788 s, 750 s, 600 w, 590 w. ^{1}H NMR (ppm, C_6D_6): 1.17 (t, 12 H, $N(CH_2C\mathit{H}_3)_2$), 1.18 (d, 24 H, $CH(C\mathit{H}_3)_2$), 3.84 (q, 8 H, $N(C\mathit{H}_2CH_3)_2$), 3.88 (sept, 4 H, $C\mathit{H}(CH_3)_2$), 6.85-7.10 (m, 6 H, aryl).

Bis((2,6-diisopropylphenyl)imido)bis((2,6-diisopropylphenyl)amido)molybdenum(VI) (7). A mixture of 371 mg of dichloro derivative 1 (0.97 mmol) and 365 mg of lithium (2,6-diisopropylphenyl)amide monoetherate (2.0 mmol) was stirred in pentane for 12 h. Filtration of liberated LiCl and evaporation gave a deep red powder that was recrystallized from pentane at -40 °C, from which crystals suited for an X-ray analysis were obtained. IR (cm^{-1}): 3323 w, 3040 w, 1580 w, 1350 m, 1315 m, 1265 m, 1252 m, 1235 m, 849 w, 835 w, 789 w, 742 s. ^{1}H NMR of crystals (ppm, C_6D_6): 1.02 (d, 24 H, $CH(C\mathit{H}_3)_2$), 1.25 (d, 24 H, $CH(C\mathit{H}_3)_2$), 3.40 (sept, 4 H, $C\mathit{H}(CH_3)_2$), 3.85 (sept, 4 H, $C\mathit{H}(CH_3)_2$), 6.93 (m, 6 H, aryl), 7.08 (m, 6 H, aryl), 8.04 (br s, 2 H, NH).

Crystal Structure Determination. Red crystals were obtained from pentane at -40 °C and were mounted at low temperature under an inert atmosphere. Data were collected on a Philips PW1100/16 diffractometer equipped with a low-temperature device using nickel-filtered Cu Kα radiation (λ = 1.5418 Å) and a $\theta/2\theta$ flying step-scan method. No significant changes were observed for three standard reflections, which were monitored hourly during the data collection period. The Enraf-Nonius SDP package[8] was used for all calculations, except that a local data reduction program was employed. The initial step-scan data were converted to intensities by the method of Lehmann-Larson[9] and then corrected for Lorentz polarization and absorption factors, the latter computed by the method of Wacker and Stuart.[10] The structure was solved by using the heavy-atom method. Difference Fourier maps revealed maxima at positions expected for hydrogen atoms H'1 and H'2 attached to N3 and N4; these hydrogen atoms were introduced and refined by using a riding model. All other hydrogen atoms were introduced in structure factor calculations by their computed coordinates (C-H = 0.95 Å) and isotropic structure factors such that $B(H) = 1 + B_{eqv}(C)$ Å^2 and were not refined. Final difference maps revealed no significant maxima.

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Supplementary Material Available: Tables of bond lengths and angles, anisotropic thermal parameters, and hydrogen atom coordinates (8 pages); a table of observed and calculated structure factors (17 pages). Ordering information is given on any current masthead page.

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Polymeric Mercury Complexes with One-Dimensional Chain Structures. 2. Synthesis and Crystal Structure of $[\{Hg(CH_2P(O)Ph_2)_2\}_2BrLi]_n$

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Summary: An organomercury complex formulated as $[\{Hg(CH_2P(O)Ph_2)_2\}_2Br^-Li(THF)_4^+]$ (I) was obtained by the reaction of $LiCH_2P(O)Ph_2$ with $HgBr_2$ in THF. Slow evaporation of a solution of I afforded $[\{Hg(CH_2P(O)Ph_2)_2\}_2BrLi]_n$ (II), which has a one-dimensional chain structure in the solid state.

There are a number of linear one-dimensional chain complexes of heavy metals such as Au or Hg. In the case of Au, these complexes are usually homometallic[1] and often owe their chain structure to Au-Au interactions.[2] In the case of Hg(II), which exhibits little homophilicity, the chain structure is usually a result of bridging ligands. These ligands are commonly the conventional inorganic ligands[3] such as OH^-, O^{2-}, CN^-, or O_2^{2-}, but the use of some other

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Table I. Crystallographic Data for $[\{Hg(CH_2P(O)Ph_2)_2\}_2BrLi]_n$

formula	$C_{52}H_{48}BrLiHg_2O_4P_4$
fw	1348.8
space group	$P2_1/c$
a/Å	14.889 (2)
b/Å	15.194 (4)
c/Å	22.693 (5)
β/°	101.05 (2)
V/Å^3	5039 (2)
Z	4
d_{calc}/g cm^{-3}	1.78
size/mm	1.0 × 0.5 × 0.3
$F(000)$/e	2599
μ(Mo Kα)/cm^{-1}	71.6
radiation (Mo Kα)/Å	0.71069
T/°C	22
scan method	Wyckoff
2θ range/deg	4–45
total no. of reflns measd	7202
no of reflns, $F_o^2 \geq 3\sigma(F_o^2)$	4367
no of params refined	577
transmissn factor: max, min	0.969, 0.516
R^a	0.0415
$R_w{}^b$	0.0412
GOF^c	1.420
largest shift/esd, final cycle	0.009
largest peak/e Å^{-3}	1.02

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = \sum[w(||F_o| - |F_c||)]^{1/2}/\sum[w|F_o|]^{1/2}$; $w^{-1} = [\sigma^2|F_o| + |g|F_o^2]$; $g = 0.000\,461$. [c] $\mathrm{GOF} = [[\sum w(|F_o| = |F_c|)^2/(N_o - N_p)]]^{1/2}$.

bridges such as tetrathiafulvene has also resulted in one-dimensional chain structures.[4] Some homobimetallic chain structures have been obtained with heterobifunctional bridging ligands,[5] but this class of ligand is also suitable for the formation of heterometallic complexes. A series of interesting heterometallic Hg(II)-containing polymeric complexes has been obtained[6] by using the heterobifunctional 2-pyrrolidone ligand $(C_4H_6NO)^-$.

The heterobifunctional ligand $CH_2P(S)Ph_2^-$ (MTP$^-$) has been demonstrated to form bridges between two different late d-block metals.[7] Exploring the chemistry of its oxygen analogue,[9] $CH_2P(O)Ph_2^-$ (MOP$^-$) also is of interest since this ligand could reasonably be expected to form bridges through oxygen and carbon coordination between late d-block heavy metals and early d-block or s-block metals. The Sn(IV) complex, $[Ph_2Sn(MOP)Cl]_2$, which contains Sn(IV) atoms bridged by the MOP ligand has recently been structurally characterized in our group.[8] A reproducible synthesis of this complex has not yet been developed. Here we report the synthesis and structure of $[\{Hg(MOP)_2\}_2BrLi]_n$.

Results and Discussion

The reaction of a tetrahydrofuran (THF) solution of $HgBr_2$ with a THF/diethyl ether solution of Li(MOP)[9]

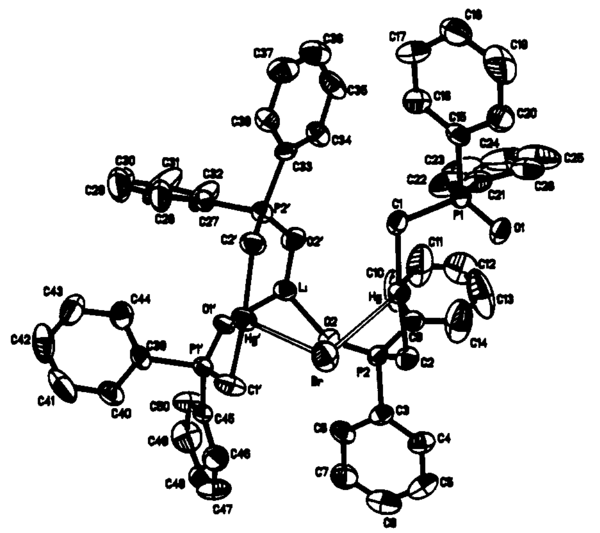

Figure 1. $[\{Hg(MOP)_2\}_2BrLi]$ unit in $[\{Hg(MOP)_2\}_2BrLi]_n$, showing 40% thermal ellipsoids and the labeling scheme.

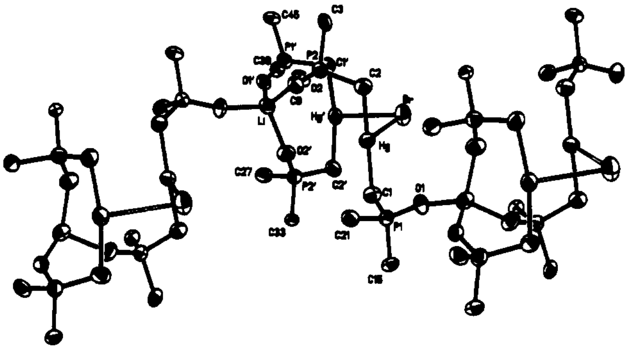

Figure 2. Extended chain structure of $[\{Hg(MOP)_2\}_2BrLi]_n$ (40% ellipsoids). A $[\{Hg(MOP)_2\}_2BrLi]_3$ unit is represented.

afforded a colorless solid, formulated as $[\{Hg(MOP)_2\}_2Br^-Li(THF)_4{}^+]$ (I) on the basis of ^1H NMR and IR spectroscopies and elemental analysis, in 67% yield. The recrystallization of this complex from THF/CH_2Cl_2/$CHCl_3$ solution by slow evaporation gave colorless crystalline $[\{Hg(MOP)_2\}_2BrLi]_n$ (II) in 75% yield (51% from $HgBr_2$). The loss of THF ligands on recrystallization was inferred from the loss of ^1H NMR signals attributable to THF, on going from I to II.

The structure of II was determined by single-crystal X-ray diffraction analysis. Table I contains some salient crystallographic data, Table II gives atomic coordinates along with their associated isotropic thermal parameters, Table III contains selected bond lengths, and Table IV contains selected bond angles. The structure is represented in Figure 1. It contains two distinct types of $\{Hg(MOP)_2\}$ fragment, one bridging two Li^+ ions and one chelating a Li^+ ion. In this way, each Li^+ is tetrahedrally coordinated. There is also a Br^- anion bridging between each proximal pair of chelating and bridging $\{Hg(MOP)_2\}$ moieties. As a result of the bridging between Li^+ cations, the whole structure consists of infinite linear chains. This is shown in Figure 2, the hydrogen atoms having been omitted and phenyl rings represented only by their 1-position carbon atoms, for clarity.

As expected, the $\{MOP\}$ ligands bond to Hg(II) via their carbon atoms, forming a nearly linear C–Hg–C arrangement. The known coordinative flexibility of Hg(II)[5] lends the metal to weak interactions with bases. The Hg–Br interactions in this complex are weak and probably largely electrostatic. Their weakness is evident from the long

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Table II. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^3)[a] for [{Hg(MOP)$_2$}$_2$BrLi]$_n$

atom	x	y	z	U_{iso}[b]
Hg	473 (1)	795 (1)	2680 (1)	47 (1)
Hg′	2591 (1)	−285 (1)	3989 (1)	53 (1)
Br	2106 (1)	1577 (1)	3655 (1)	71 (1)
P1	−1605 (2)	1178 (2)	2803 (1)	41 (1)
P1′	3994 (2)	−1536 (2)	3567 (1)	46 (1)
P2	1764 (2)	−196 (2)	1881 (1)	44 (1)
P2′	851 (2)	−1414 (2)	3958 (1)	44 (1)
O1	−1534 (5)	2075 (4)	2550 (3)	51 (3)
O1′	3141 (5)	−2045 (4)	3340 (3)	48 (3)
O2	2108 (5)	−804 (5)	2389 (3)	59 (3)
O2′	927 (5)	−1458 (5)	3314 (3)	56 (3)
Li	1888 (13)	−1824 (13)	2853 (8)	48 (7)
C1	−545 (8)	761 (8)	3221 (5)	52 (5)
C1′	3808 (8)	−384 (8)	3646 (6)	67 (5)
C2	1387 (8)	847 (7)	2073 (4)	49 (4)
C2′	1353 (8)	−456 (7)	4321 (5)	57 (5)
C3	2679 (8)	52 (7)	1472 (5)	47 (4)
C4	2625 (9)	711 (7)	1038 (5)	58 (5)
C5	3321 (12)	899 (9)	740 (6)	82 (7)
C6	4101 (11)	411 (11)	886 (7)	93 (8)
C7	4198 (10)	−287 (10)	1290 (6)	79 (6)
C8	3470 (8)	−456 (8)	1594 (6)	60 (5)
C9	839 (8)	−674 (7)	1358 (5)	51 (4)
C10	602 (12)	−1487 (10)	1407 (8)	152 (10)
C11	−109 (16)	−1899 (12)	989 (11)	195 (14)
C12	−575 (13)	−1510 (10)	548 (8)	106 (9)
C13	−410 (14)	−695 (13)	524 (9)	161 (11)
C14	288 (15)	−259 (12)	904 (9)	165 (11)
C15	−2437 (7)	1140 (8)	3298 (5)	46 (4)
C16	−2466 (8)	480 (7)	3710 (5)	55 (5)
C17	−3073 (9)	448 (8)	4076 (6)	69 (6)
C18	−3732 (10)	1102 (11)	4041 (6)	79 (6)
C19	−3738 (11)	1780 (12)	3633 (7)	101 (8)
C20	−3067 (9)	1832 (9)	3265 (5)	67 (6)
C21	−2056 (8)	401 (8)	2224 (5)	53 (5)
C22	−1680 (11)	−431 (7)	2163 (6)	77 (6)
C23	−2075 (13)	−982 (10)	1719 (7)	118 (9)
C24	−2825 (13)	−717 (11)	1312 (7)	131 (9)
C25	−3179 (11)	88 (11)	1347 (6)	111 (8)
C26	−2811 (9)	666 (9)	1787 (5)	70 (6)
C27	1365 (8)	−2360 (8)	4365 (5)	53 (5)
C28	1760 (10)	−2332 (10)	4977 (6)	88 (7)
C29	2100 (11)	−3101 (11)	5264 (7)	106 (8)
C30	2098 (10)	−3853 (11)	4979 (7)	108 (8)
C31	1718 (14)	−3883 (10)	4366 (8)	138 (11)
C32	1357 (11)	−3120 (7)	4059 (6)	81 (7)
C33	−335 (7)	−1522 (7)	4033 (4)	40 (4)
C34	−968 (8)	−1853 (7)	3574 (5)	55 (5)
C35	−1875 (8)	−1991 (7)	3656 (6)	69 (5)
C36	−2114 (10)	−1825 (8)	4197 (7)	74 (6)
C37	−1488 (10)	−1490 (9)	4644 (7)	72 (6)
C38	−601 (8)	−1328 (8)	4588 (6)	64 (5)
C39	4545 (7)	−1936 (7)	4295 (5)	49 (4)
C40	5359 (8)	−1594 (9)	4596 (6)	68 (5)
C41	5760 (10)	−1910 (11)	5150 (6)	99 (7)
C42	5391 (11)	−2597 (11)	5389 (6)	91 (7)
C43	4612 (12)	−2916 (11)	5112 (6)	87 (7)
C44	4155 (9)	−2612 (8)	4550 (5)	64 (5)
C45	4849 (7)	−1747 (7)	3104 (4)	44 (4)
C46	5361 (10)	−1110 (9)	2901 (7)	81 (6)
C47	5993 (10)	−1312 (11)	2562 (7)	95 (7)
C48	6121 (10)	−2139 (11)	2388 (6)	82 (7)
C49	5680 (11)	−2792 (12)	2613 (7)	96 (8)
C50	4973 (9)	−2600 (9)	2960 (6)	77 (6)

[a] Estimated standard deviations in the least significant digits are given in parentheses. [b] The equivalent isotropic U is defined as one-third of the trace of the $\mathbf{U}_{ij}$ tensor.

Table III. Bond Lengths (Å)[a] for [{Hg(MOP)$_2$}$_2$BrLi]$_n$

Hg–Br	3.187 (1)	Hg–C1	2.125 (12)
Hg–C2	2.116 (12)	P2′–C33	1.813 (11)
P2′–C2′	1.767 (11)	P2′–O2′	1.489 (8)
P2′–C27	1.798 (12)	Hg′–C1′	2.110 (14)
Hg′–Br	2.981 (1)	Hg′–C2′	2.136 (13)
P1–C21	1.798 (11)	P1–O1	1.490 (7)
P1–C1	1.794 (11)	P1–C15	1.825 (13)
Li–O1a	1.932 (20)	P1′–C1′	1.786 (12)
P1′–O1′	1.492 (7)	P1′–C45	1.827 (12)
P1′–C39	1.804 (11)	O1′–Li	2.007 (19)
P2–C3	1.828 (13)	P2–C2	1.763 (12)
P2–O2	1.489 (8)	P2–C9	1.791 (11)
O2–Li	1.937 (21)	O2′–Li	2.006 (22)

[a] Estimated standard deviations in the least significant digits are given in parentheses.

Table IV. Bond Angles (deg)[a] for [{Hg(MOP)$_2$}$_2$BrLi]$_n$

Br–Hg–C1	98.2 (3)	Br–Hg–C2	86.4 (3)
C1–Hg–C2	174.7 (4)	Hg′–C1′–P1′	105.5 (6)
C33–P2′–C2′	111.3 (5)	C33–P2′–O2′	110.4 (5)
C2′–P2′–O2′	112.9 (5)	C33–P2′–C27	101.9 (5)
C2′–P2′–C27	108.5 (5)	O2′–P2′–C27	111.3 (5)
C1′–Hg′–Br	99.0 (3)	Br–Hg′–C2′	91.3 (3)
C21–P1–O1	111.3 (5)	C21–P1–C1	108.7 (5)
O1–P1–C1	114.0 (5)	C21–P1–C15	103.1 (6)
O1–P1–C15	111.9 (5)	C1–P1–C15	107.3 (5)
O1′–Li–O2	101.4 (9)	O1′–Li–O2′	116.1 (9)
O2–Li–O2′	105.8 (9)	O1′–Li–O1a	104.9 (9)
O2–Li–O1a	119.7 (10)	O2′–Li–O1a	109.3 (10)
P1–O1–Lia	160.3 (8)	C1′–P1′–O1′	113.8 (5)
C1′–P1′–C45	111.6 (6)	O1′–P1′–C45	110.5 (5)
C1′–P1′–C39	106.9 (6)	O1′–P1′–C39	110.5 (5)
C45–P1′–C39	102.9 (5)	Hg–C1–P1	109.8 (5)
Hg–C2–P2	113.7 (6)	Li–O1′–P1′	138.1 (7)
C3–P2–C2	104.1 (5)	C3–P2–O2	109.9 (5)
C2–P2–O2	116.4 (5)	C3–P2–C9	107.5 (5)
C2–P2–C9	106.7 (5)	O2–P2–C9	111.6 (5)
P2′–C2′–Hg′	104.6 (6)	Li–O2–P2	148.0 (7)
P2′–O2′–Li	136.1 (7)		

[a] Estimated standard deviations in the least significant digits are given in parentheses.

Hg–Br distances of 3.187 (1) and 2.981 (1) Å. These are longer than the sum of the atoms' covalent radii, about 2.65 Å,[10] and far longer than the typical Hg–Br distance of 2.441 (5) Å in a fully covalently bonded complex such as $\mathrm{HgBrCH_2C(O)CH_3}$.[11] The weakness of the Hg–Br interaction is further demonstrated by the C–Hg–C angles of 174.7 (4) and 168.9 (4)°, which are little distorted from the expected linearity of a 2-coordinate Hg(II) atom. There appear to be no other close contacts, intramolecular or intermolecular, between Hg atoms and other atoms in the structure.

There are a few other (sp^3)C—P=O ligands with structurally characterized metal complexes.[12-14] The dinuclear complex [Ph$_2$SnCl(MOP)]$_2$ has been characterized recently in our laboratory.[8] Of these structures, all except two[14] seem to involve some degree of interaction between the P=O oxygen atoms and a metal center. The complex [PtCl$_2$(PEt$_3$)CH{CH$_2$P(O)Ph$_2$}$_2$Li]$_2$ contains P=O coordinated Li$^+$,[12] but the errors associated with bond lengths reported for this structure are large, so comparisons therewith are not meaningful. Excluding this structure, the mean P—C bond length of the other M—(sp^3)C—P=O containing structures[15] is 1.774 (4) Å and the mean P=O distance is 1.476 (4) Å. The mean P—(sp^3)C and P=O bond lengths in II are 1.778 (6) and 1.490 (4) Å,

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(15) That is, of [Hg(NO$_3$)CH{P(O)(OEt)$_2$}$_2${CONEt$_2$}]$_2$, *cis*- and *trans*-[PtI(PPh$_3$)$_2$CH$_2$P(O)(OMe)$_2$], and [SnPh$_2$Cl(MOP)]$_2$.

respectively. Another instructive comparison is with the one-dimensional chain structure observed for $Hg(MTP)_2$.[5] This closely analogous sulfur complex has Hg–C and P–(sp^3)C bond lengths of 2.124 (16) and 1.771 (22) Å, respectively, which correspond closely to those in II, of 2.122 (6) and 1.778 (6) Å.

The tetrahedral coordination geometry around Li^+ is slightly distorted; the six O–Li–O angles range from 101.4 (9) to 119.7 (10)°, with the Li–O distances ranging from 1.932 (20) to 2.007 (19) Å, mean 1.971 (10) Å. These are fairly long for this type of bond, but not unprecedentedly so. The mean Li–O distance in $\{LiN(CH_2CH_2P(O)Ph_2)_3\}^+$, in which the Li is 3-coordinate, is 1.85 (3) Å,[16] yet in $[Li_2(H_2O)_4\{O{=}P(NMe_2)_3\}_2]^{2+}$, the Li–O distance is 1.999 (2).[17] The eight-membered Hg–C–P–O–Li–O–P–C ring, which adopts a somewhat twisted boat conformation, appears to contain no unduly acute angles at any of the member atoms.

The ^1H NMR spectra of I and II are consistent with their proposed formulations and the crystal structure of II. The signal originating from the methylene protons, at 2.04 ppm, shows a small (9 Hz) coupling to ^{31}P and a larger (157 Hz) coupling to ^{199}Hg, the latter giving rise to two small satellite peaks. No coupling to ^{201}Hg is observed. The spectra of I and II are identical except for the presence in I of signals corresponding to 4 equiv of THF. These signals are absent in II. Addition of pure THF to the NMR sample solution of I induces little chemical shift change of the signals and no visible change in the resolution, such as would be caused by a coalescence of signals from free and from coordinated THF.

The IR spectra of I and II are unremarkable except with respect to their P=O stretching bands. Those of I occur at 1180 and 1155 cm^{-1}. In II, these appear to have been replaced by a single broad band at 1175 cm^{-1}. It is possible that this difference is attributable to coordination differences between I and II in the solid state. It is apparent from Figure 2 that at least four environments are found for the P=O groups in the solid-state structure of II. It is likely that the near-coincidence of their IR absorption frequencies could result in the broad band at 1175 cm^{-1}.

Experimental Section

All solvents were freshly dried by distillation from standard drying agents under nitrogen, prior to use. All reactions were carried out under a purified nitrogen atmosphere, unless stated. No special precautions against photolysis were taken. ^1H NMR spectra were recorded by using a Varian XL-200 spectrometer at 200 MHz. IR spectra were recorded by using a Perkin-Elmer Model 783 spectrometer. Elemental analyses were performed by Texas Analytical Laboratories.

Synthesis of [$\{Hg(MOP)_2\}_2Br^-Li(THF)_4^+$] (I). $HgBr_2$ (0.721 g, 2.00 mmol) and triphenylphospine oxide (1.161 g, 4.17 mmol) were placed in separate 50-mL Schlenk flasks, each containing a stirring bar. They were dried in vacuo for 1 h, whereupon 7 mL of tetrahydrofuran was added to the $HgBr_2$ and 5 mL to the phosphine oxide under nitrogen. After a few minutes of stirring to effect dissolution, the phosphine oxide solution was placed in a dry ice/acetone bath and 2.95 mL of a 1.4 M solution of methyllithium in diethyl ether (4.1 mmol) was added by using a syringe. The cold bath was removed from the pale yellow mixture, and stirring was resumed, as the flask was allowed to warm to room temperature. A deep red color was observed after 30 min. After 90 min, the $HgBr_2$ solution was cooled in a dry ice/acetone bath and the Li(MOP) solution was added dropwise, via a cannula, with stirring. Upon completion of the addition, the flask formerly containing the Li(MOP) solution was rinsed with 2 × 0.5 mL of THF, the washings also being added to the $HgBr_2$ solution. The cold bath was removed from the resulting red[18] solution and the solvent was evaporated by reduced pressure. When its volume had fallen to ca. 10 mL, it was warmed to room temperature and stirred under nitrogen for 1 h. After this time, it was stored at −20 °C overnight, which resulted in the formation of a pale precipitate and an amber solution. The solution was cooled in a dry ice/acetone bath for 1 h, after which the supernatant was carefully removed by using a cannula and the residue washed with 2 × 1 mL of THF and then dried in vacuo (1.09 g, 67% yield). ^1H NMR ($CDCl_3$, δ, ppm): 1.83 (m, 16 H, THF), 2.04 (d, 4 H, $^2J_{Hg-H}$ = 157 Hz, $^2J_{P-H}$ = 9 Hz), 3.73 (m, 16 H, THF), 7.05 (m, 8 H), 7.28 (t, 4 H), 7.53 (q, 8 H). Anal. Calcd for $C_{68}H_{80}BrLiHg_2O_8P_4$: C, 49.88; H, 4.92; Br, 4.88; Li, 0.42. Found: C, 48.48; H, 5.02; Br, 4.83; Li, 0.37. IR (KBr dispersion, cm^{-1}): 1155 and 1180. Mp: decrepitation, 145–155 °C.

Synthesis of [$\{Hg(MOP)_2\}_2BrLi]_n$ (II). I (1.09 g, 0.668 mmol) was dissolved in a mixture of 2 mL of THF, 2 mL of CH_2Cl_2, and 3 mL of $CHCl_3$. The solution was centrifuged until clear, and the supernatant was transferred, in air, to a test tube and plugged with paper tissue.[21] A precipitate continued to form and was periodically removed, over several days, by the centrifugation of the solution followed by the transfer of the supernatant to a fresh tube to continue the process of evaporation. Once crystallization of II ensued, the formation of the precipitate was negligible. When the volume of the solution had fallen to ca. 1 mL, it was removed, and the crystals were washed with 2 × 1 mL of 50:50 CH_2Cl_2:hexane and dried in vacuo (0.714 g, 79% yield). Anal. Calcd for $C_{52}H_{48}BrLiHg_2O_4P_4$: C, 46.21; H, 5.62; Br, 6.01; Li, 0.57. Found: C, 46.30; H, 3.59; Br, 5.92; Li, 0.51. IR (KBr dispersion, cm^{-1}): 1175 (br). Mp: 145–155 °C.

X-ray Crystallography. A crystal of II was mounted on a glass fiber by using epoxy resin and the whole was then placed inside a capillary containing a small amount of mother liquor. The capillary was flame sealed.[19] The unit cell was determined using 25 reflections in the range $21 < 2\theta < 30°$, using a Nicolet R 3m/E diffractometer controlled by a Data General Nova 4 computer. Data were collected at ambient temperature by using graphite-monochromated Mo Kα radiation, over the range $4 < 2\theta < 45°$ (h, 0 to 12; k, 0 to 12; l, −18 to 18), using the Wyckoff method. They were subsequently corrected for Lorentz and polarization effects and for random small fluctuations in the intensities of 3 check reflections surveyed every 97 scans. An empirical absorption correction was applied on the basis of azimuthal scans.

Data processing was performed on a Data General Eclipse S 140 computer using SHELXTL 5.1.[20] Hg atoms were located by using direct methods, and all other non-hydrogen atoms were located by using subsequent Fourier maps. All non-hydrogen atoms were refined anisotropically, with all hydrogens being placed in idealized positions at a distance of 0.96 Å from their parent carbon atoms, for the last cycles of refinement.

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Supplementary Material Available: Tables listing anisotropic thermal parameters and hydrogen atom coordinates for $[\{Hg(MOP)_2\}_2BrLi]_n$ (5 pages); a table of calculated and observed structure factors for $[\{Hg(MOP)_2\}_2BrLi]_n$ (27 pages). Ordering information is given on any current masthead page.

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(18) Reasonable results have also been obtained with solutions that were amber in color.

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