likely forms an adduct with I_2. Such a process would account for the formation of the kinetic products **2**-*cis* and **4**-*trans*. The formation of the kinetic complexes **4**-*trans* and **2**-*cis* from **3a** possibly occurs in two steps. For such a mechanism, a reductive elimination of $HOs(CO)_4I$ should take place in a stereospecific manner and should yield the kinetic product **4**-*trans* and, concomitantly, the dinuclear complex $Os_2(CO)_6(OCNHR)(\mu\text{-}I)$ (**5**). The concerted addition of I_2 across the metal-metal bond of the complex **5** should then produce the dinuclear complex **2**-*cis*. In support of the proposed mechanism, it is significant that, in the absence of I_2, **3b** slowly decomposes in about 20 days, producing complex **5** in a moderate yield, and that the reaction of **5** with I_2 quickly affords **2**-*cis* (see Scheme I). A single-step process from **3a** to **2**-*cis* cannot be ruled out, even though it is less likely.

In conclusion, the addition of I_2 to the triosmium cluster demonstrates the influence of the oxygen atom of the unsymmetrically bonded carboxamido ligand upon the cleavage of the Os-Os bond. Moreover, the stereospecificity of the products provides evidence for a concerted additions of I_2. I_2 addition to similar clusters with one or more unsymmetrical bridging ligands is currently under investigation.

Experimental Section

General Conditions. Standard inert-atmosphere techniques were used for the manipulation of all reagents and reaction products. Infrared spectra were recorded on a Perkin-Elmer Model 983 spectrometer. The ^1H and ^{13}C NMR spectra were taken on a Bruker AM-300WB spectrometer at ambient temperature. Electron impact mass spectra were recorded on a JEOL JMS D-300 spectrometer. Solvents were rigorously dried with appropriate drying agents and distilled before use. $HOs_3(CO)_{10}(OCNHR)$ was prepared by literature methods.[1]

Isolation of $HOs_3(CO)_{10}(OCNHCHMe_2)I_2$ (3b). To a solution of 373 mg (0.40 mmol) of $HOs_3(CO)_{10}(OCNHR)$ in 10 mL of acetone, in an ice bath, was added 143 mg of I_2. The solution was stirred at ambient temperature for 4 h, during which time a white precipitate was apparent. Filtration of the mixture afforded **2**-*cis*, as a white powder. The solvent of the filtrate was removed under vacuum, and the residue was extracted with hexane (4 × 15 mL). The volume of hexane was reduced to about 5 mL; then the mixture was passed through a silica gel packed column by using 30% dichloromethane-70% hexane as the eluent. The yellow product (second band, 70 mg; 15%) was recrystallized from hexane. ^1H NMR ($CDCl_3$): δ 5.88 (d, broad doublet, 1 H, NH), 4.22 (m, 1 H, CH), 1.18 (dd, 6 H, 2 Me), −16.9 (s, 1 H, hydride). ^{13}C NMR ($CDCl_3$): δ 170.51 (carboxamido C), 184.18, 182.76, 176.31, 175.43, 175.38, 169.94, 166.65, 165.13, 163.30, 160.82 (10 terminal CO's), 44.75 (CH), 23.06, 22.48 (2 Me). IR (ν_{CO}, in C_2Cl_4, cm^{-1}): 2125 (w), 2115 (m), 2082 (m), 2043 (s), 2025 (m), 2018 (w, sh), 2005 (m), 1999 (w), 1986 (w). Mass spectrum: parent peak observed at *m/e* 1195; peaks attributed to each of the 10 CO losses also observed at *m/e* 1166, 1138, 1110, 1082, 1054, 1026, 998, 970, 942, and 914, respectively. Anal. Calcd for **3b**: C, 14.06; H, 0.75. Found: C, 14.39; H, 0.68.

Structure Determination of 3b. Crystals of **3b** were grown from hexane as yellow cubes. The dimensions of the crystal chosen for X-ray diffraction were 0.50 × 0.48 × 0.38 mm. This crystal was mounted on a CAD4 four-circle diffractometer, and intensities were collected for $4 < 2\theta < 50°$ according to the methods described earlier.[1] The data were processed with the following lattice parameters: $a = 9.030$ (6) Å, $b = 24.522$ (4) Å, $c = 11.783$ (4) Å, $\beta = 105.59$ (4)°. The space group, based on the systematic absences, was uniquely assigned as $P2_1/n$. The volume was 2513 (2) Å^3, and the calculated density was 3.174 g/cm^3. Of the total 4708 reflections, 3089 independent intensities having $I > 2.5\sigma(I)$ were deemed "observed", and only these were used in the solution and refinement of the structure. Data were corrected for Lorentz-polarization effects, and an empirical absorption correction was applied on the basis of azimuthal rotation. The iodine and osmium atoms were located by Patterson methods, and the carbon, oxygen, and nitrogen atoms were located by successive electron-density difference syntheses. Two CO ligands, CO(2D) and CO(3D), and two iodine ligands were disordered and were refined with partial occupancies. The structure was refined by full-matrix least squares with anisotropic thermal parameters for all the non-hydrogen atoms except those disordered CO's. The refinement converged to $R = 0.043$ and $R_w = 0.032$. All intramolecular bond distances and angles are within normal ranges except those in disorder.

Isolation of $Os_2(CO)_6(OCNHCHMe_2)(\mu\text{-}I)$ (5). Complex **3b** (30 mg, 0.025 mmol), isolated as described above, was stored under nitrogen in $CHCl_3$ for ca. 20 days, during which time transformation of complex **3b** to **5** took place. Complex **5** was also purified by column chromatography (second band) by using 30% dichloromethane-70% hexane as eluent (7 mg, 36%). ^1H NMR ($CDCl_3$): δ 5.52 (d, broad doublet, 1 H, NH), 3.97 (m, 1 H, CH), 1.05 (dd, 6 H, 2 Me). ^{13}C NMR ($CDCl_3$): δ 185.52 (carboxamido C), 179.02, 176.66, 176.59, 176.22, 175.90, 174.05 (6 terminal CO's) 43.10 (CH), 22.67, 22.36 (2 Me). Mass spectra show a parent ion envelope (*m/e* 765) accompanied by six envelopes corresponding to successive losses of CO from the parent ion.

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Supplementary Material Available: Listings of crystal and intensity collection data, fractional coordinates, isotropic thermal parameters, and complete bond distances and bond angles for **3b** (5 pages); a listing of observed and calculated structure factors for **3b** (15 pages). Ordering information is given on any current masthead page.

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^{207}Pb NMR Study on Transition-Metal-Substituted Organolead Complexes

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Summary: Chemical shift and coupling constant data for a variety of trimethyl-, triethyl-, and triphenyllead complexes of the transition-metal systems $Mn(CO)_5$, $(\eta^5\text{-}C_5H_5)M(CO)_n$ (M = Fe, Cr, Mo, W), and $Co(CO)_4$, and some of their phosphine-substituted derivatives, are reported. The variations in chemical shift closely resemble ^{119}Sn data obtained from a similar, but limited, set of Sn complexes but are somewhat more sensitive to chemical substitution on the lead atom. Changes in solvent and concentration do not produce major changes in chemical shift, suggesting that neither coordination by polar solvents nor self-association in solution are important in this series of complexes.

The synthesis of stable lead-metal complexes was published as early as 1941 by Hein and co-workers[1] and later by several other groups.[2-4] In general the complexes reported were stable crystalline materials of limited chem-

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Table I. Chemical Shift Data for Lead–Transition Metal Complexes

complex	δ	${}^nJ_{X\text{-}Pb}$, Hz	$\Delta\nu_{1/2}$, Hz
1 $(\eta^5\text{–}C_5H_5)Fe(CO)_2PbEt_3$	398.9		
2 $(\eta^5\text{-}C_5H_5)Fe(CO)_2PbMe_3$	245.6		
3 $(\eta^5\text{-}C_5H_5)Fe(CO)_2PhPh_3$	125.1		
4 $(\eta^5\text{-}C_5H_5)Cr(CO)_3PbEt_3$	423.1		
5 $(\eta^5\text{-}C_5H_5)Cr(CO)_3PhMe_3$	360.2	$n = 2$, X = H, 43	
6 $(\eta^5\text{-}C_5H_5)Cr(CO)_3PbPh_3$	210.1		
7 $(\eta^5\text{-}C_5H_5)Mo(CO)_3PbEt_3$	311.8		
8 $(\eta^5\text{-}C_5H_5)Mo(CO)_3PbMe_3$	220.5	$n = 2$, X = H, 44	
9 $(\eta^5\text{-}C_5H_5)Mo(CO)_3PbPh_3$	115.6		
10 $(\eta^5\text{-}C_5H_5)W(CO)_3PbEt_3$	29.2	$n = 1$, X = W, 115	
11 $(\eta^5\text{-}C_5H_5)W(CO)_3PbMe_3$	−100.7	$n = 1$, X = W, 182; $n = 2$, X = H, 55	
12 $(\eta^5\text{-}C_5H_5)W(CO)_3PbPh_3$	−221.0	$n = 1$, X = W, 378	
13 $Co(CO)_4PbEt_3$	478.3		
14 $Co(CO)_4PbMe_3$	348.9		
15 $Co(CO)_4PbPh_3$	132.6		
16 $Mn(CO)_5PbEt_3$	230.6		180
17 $Mn(CO)_5PbMe_3$	140.0		360
18 $Mn(CO)_5PbPh_3$	55.0		600
19 $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_4Pb$	457.1		
20 $[(\eta^5\text{-}C_5H_5)W(CO)_3]_2PbEt_2$	−130.7		
21 $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)PbEt_3$	207.4	$n = 2$, X = P, 443	
22 $Co(CO)_3(PPh_3)PbEt_3$	438.4	$n = 2$, X = P, 178	
23 $Co(CO)_3(PPh_3)PbMe_3$	270.3	$n = 2$, X = P, 192	
24 $(Co(CO)_3(PPh_3)PbPh_3$	111.3	$n = 2$, X = P, 473	
25 $(\eta^5\text{-}C_5H_4PbMe_3)Mo(CO)_3Me$	−4.1		
26 $(\eta^5\text{-}C_5H_4PbPh_3)Mo(CO)_3Me$	−174.6		
27 $(\eta^5\text{-}C_5H_4PbMe_3)W(CO)_3Me$	−0.3		
28 $(\eta^5\text{-}C_5H_4PbPh_3)W(CO)_3Me$	−176.5		

istry, and this stability was used by Ellis and Faltynek for the characterization of highly reduced organometallic anions, for example, $[M(CO)_4]^{3-}$, M = Mn, Re.[5] Recently, however, Hitchen et al. postulated the intermediacy of reactive Pb–Zn complexes during the Zn-catalyzed removal of organolead compounds from aqueous environments.[6] The mechanism proposed involved alkyl migrations from Pb to the Zn atom in intermediates of the type Me_3PbZnX to form Me_2Pb and MeZnX, and such 1,2-alkyl and aryl migrations from Pb to Fe, Mo, W are now well established.[7-9] Such metal–lead complexes have been characterized via ^1H and ^{13}C NMR and IR spectroscopy, but whereas the use of nuclear magnetic resonance of the group 14 nuclei ^{13}C, ^{29}Si, and ^{119}Sn to study the structure, bonding, and molecular mobility of transition-metal complexes of C, Si, and Sn is well established,[10-12] reports on the use of ^{207}Pb NMR to study metal–lead complexes are scarce. Using ^{207}Pb NMR, Carr et al. showed that the intermediate formed during the synthesis of *cis*-$Pt(PPh_3)_2Ph(PbPh_3)$ from $Pt(PPh_3)_2C_2H_4$ and Ph_6Pb_2 was *cis*-$Pt(PPh_3)_2Ph(Pb_2Ph_5)$ and not $Pt(PPh_3)_2(PbPh_3)_2$ as previously suggested.[13,14] Related to such utility is a report by Wilson et al. concerning the characterization of anionic clusters of main-group elements including Sn, Pb, Ge, and Tl using, inter alia, ^{207}Pb NMR.[15] We now report the ^{207}Pb chemical shift data for a large range of transition-metal lead complexes principally containing direct metal–lead bonds but including, for comparison, a number of complexes in which the lead is bonded to an η^5-cyclopentadienyl group.

Table II. ^{207}Pb Chemical Shifts (δ) of $LMPbR_3$: Solvent Dependency

LM	C_6D_6	CH_3OH	C_5H_5N
$(\eta^5\text{-}C_5H_5)Fe(CO)_2PbEt_3$	399	395	402
$(\eta^5\text{-}C_5H_5)Mo(CO)_3PbEt_3$	312	311	319
$Mn(CO)_5PbEt_3$[a]	231	232	234
$(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)PbEt_3$[b]	207	200	207
$(\eta^5\text{-}C_5H_5)W(CO)_3PbEt_3$	29	27	40
$[(\eta^5\text{-}C_5H_5)W(CO)_3]_2PbEt_2$	−131	−150	−129
$(\eta^5\text{-}C_5H_5)W(CO)_3PbMe_3$[c]	−101		−88
$(\eta^5\text{-}C_5H_5)W(CO)_3PbPh_3$[d]	−221		−214

[a] Line width at half-height (Hz): C_6D_6 = 180, CH_3OH = 152, C_5H_5N = 133. [b] ^2J(Pb–P) (Hz): C_6D_6 = 433, CH_3OH = 444, C_5H_5N = 443. [c] ^1J(Pb–W) (Hz): C_6D_6 = 182, C_5H_5N = 171. [d] ^1J(Pb–W) (Hz): C_6D_6 = 378, C_5H_5N = 392.

Experimental Section

The various complexes were synthesized by literature procedures.[1-4,7-9] In all cases experimental manipulations were performed in an atmosphere of dry, oxygen-free, nitrogen or argon. NMR spectral data were recorded by using standard procedures on an IBM NR 200 multinuclear spectrometer. The ^{207}Pb chemical shift data are reported relative to $PbMe_4$ at 0.0 ppm, where a positive sign indicates a shift to low frequencies of $PbMe_4$ and a negative sign a shift to high frequency. All chemical shift data have an uncertainty of ±0.2 ppm.

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The ^{207}Pb chemical shift data for 28 transition-metal-substituted organolead complexes are recorded in Table I. Representative data from eight of these complexes are recorded as a function of varying solvent (C_6D_6, CH_3OH, and C_5H_5N) in Table II. The range of chemical shifts is large, from +478 ppm for $Co(CO)_3(PPh_3)(PbEt_3)$ to -221 ppm for $(\eta^5\text{-}C_5H_5)W(CO)_3PbPh_3$.

Results and Discussion

The observation of the ^{207}Pb resonances in the series of complexes studied presented no problems, and both the ^{1}H-coupled and decoupled spectra were readily obtained. The data recorded in the tables indicate that for the complexes LM–PbR_3, the nature of the organic substituents, R, and the transition metal, LM, has a large effect upon the chemical shift of the lead nucleus.

Our study concentrated upon the three organic substituents ethyl (Et), methyl (Me), and phenyl (Ph). For a given transition-metal system, the Et_3Pb resonances occur consistently about 100 ppm to low frequency of the Me_3Pb resonances, which in turn occur about 100 ppm to low frequency of those of the Ph_3Pb complexes. Such results are in accord with the limited data published on ^{207}Pb chemical shifts of organolead compounds.[16,17] For example, Me_3PbI has a ^{207}Pb resonance at 203 ppm, while that for Et_3PbI is at 303 ppm, Ph_3PbEt at -114 ppm, and Ph_4Pb at -170 ppm.[16]

Variations of the ^{207}Pb chemical shifts as a function of the transition metal are large, reflecting a range of 650 ppm. The metal complexes used are all low-valent carbonyl-containing systems, some of them also containing the $\eta^5\text{-}C_5H_5$ ligand. There is no clear statement to be made concerning the order of the chemical shift for a particular R_3Pb group; however, it is interesting to note that the trends are very consistent with the relative changes observed for both ^{29}Si and ^{119}Sn resonances for those Si and Sn complexes of the same transition-metal complexes where comparisons are possible. From these limited data it appears that the third-row transition metals exert a well-defined high-field shift. This has been interpreted by Harris et al. as deriving from a combination of reduction in π-bonding between Sn and the transition metal and a greater polarizability of the third-row element.[12]

The data in Table I suggests that the ^{207}Pb resonances are about 3 times as sensitive as the ^{119}Sn resonances to substituent effects. Theoretical predictions suggest that for related four-coordinate lead and tin compounds this number should be 1.4.[18] This same discrepancy between concept and reality has been previously noted for a comparable series of organolead and -tin compounds, and thus the transition-metal substituents do not dramatically change the distinction between the two group 14 metals.[16]

For some of the transition-metal–carbonyllead complexes we were able to synthesize phosphine derivatives. ^{207}Pb NMR data from these complexes (Table II) illustrate that substitution of a CO ligand by PPh_3 causes a high-frequency shift. The extent of this shift varies as a function of the metal involved and the organic substituent upon lead. For the series of $Co(CO)_4$– and $Co(CO)_3(PPh_3)$–PbR_3 complexes the shifts are relatively small, i.e., 39 (R = Et) and 24 ppm (R = Me and Ph). On the other hand, for the complexes $(\eta^5\text{-}C_5H_5)Fe(CO)(L)PbEt_3$, L = CO, PPh_3, the shift is large, 192 ppm. In general, the replacement of a CO ligand by PPh_3 is thought to increase the nucleophilicity of the metal atom, thereby increasing the capacity of the metal to undertake retrodative π-bonding. The greater effect of the PPh_3 substituent upon the Fe complexes may reflect the fact that there is only one CO ligand remaining upon phosphine substitution to participate in any π-bonding, whereas in the case of the cobalt complexes the change from four to three CO ligands does not impose so great a need for charge redistribution to the remainder of the molecule.

^{207}Pb chemical shift data obtained from complexes in which the organolead group is bonded to the cyclopentadienyl ring are similar to those obtained from organolead compounds with four organic ligands. The two $(\eta^5\text{-}C_5H_4PbMe_3)M(CO)_3Me$ complexes, M = Mo, W, exhibit ^{207}Pb resonances at -4 and 0.0 ppm, respectively, close to the value for Me_4Pb. The related Ph_3Pb complexes exhibit resonances at -174.6 (Mo) and -176.5 (W) ppm, which compare to -170 ppm for Ph_4Pb. Clearly the effect of a transition metal upon the chemical shift of the Pb nuclei is restricted to the situation containing a direct metal–lead bond. This is also in accord with related ^{29}Si and ^{119}Sn NMR data.

A major feature of interest with respect to the published data on ^{207}Pb chemical shift data is the potential effect of solvent upon the results.[16] The chemical shift for Me_3PbCl ranges from 442 ppm in CH_2Cl_2 and 258 ppm in DMSO to -47.5 ppm in HMPA. These variations are due to the coordination of the solvent to lead, thereby increasing the coordination number of the group 14 element. In our series of complexes we observed no such effect, and clearly the capacity of the solvent to coordinate lead is restricted to those compounds that contain an electronegative substituent increasing the acidity of the lead. Related to this observation is the lack of variation of chemical shift as a consequence of changing concentration of the transition-metal–lead complexes, i.e., no self-association is occurring in solution.

Addition of extra metal substituents to the Pb atom result in significantly increasing changes in chemical shift values. The data for $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_4Pb$ (457 ppm) and $[(\eta^5\text{-}C_5H_5)W(CO)_3]_2PbEt_2$ (-131 ppm) illustrate this trend.

Finally we made a limited study of the various coupling constants between the lead atom and various other nuclei in the complexes, i.e., H, P, and W in the appropriate complexes. The data are recorded in Tables I and II. In the case of the trimethyllead complexes of Cr, Mo, and W, $^2J_{H\text{-}Pb}$ values are 43, 44, and 55 Hz, respectively, significantly less than the value of 61 Hz obtained for Me_4Pb. Such results imply an overall electron releasing capacity of the metal substituent, increasing the s-electron density on the Pb atom, thereby decreasing the coupling constant. This general trend was also observed to a lesser extent for the related ^{119}Sn complexes, $^2J_{H\text{-}Sn}$ = 54 (Me_4Sn), 48.1 (Cr), 48.3 (Mo), and 48.5 Hz (W).[12]

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