Lead Complexes

Tungsten–Lead Triple Bonds: Syntheses, Structures, and Coordination Chemistry of the Plumbylidyne Complexes *trans*-$[X(PMe_3)_4W{\equiv}Pb(2,6\text{-}Trip_2C_6H_3)]$**

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Compounds containing a multiple bond between lead and another main-group element are very rare.[1] In fact, only a few diplumbenes, $[Pb_2R_4]$ (R = aryl, silyl),[2] have been isolated to date,[3,4] whereas alkenes are ubiquitous in organic chemistry. Similarly, very few transition-metal plumbanediyl (plumbylene) complexes have been reported,[5] whereas carbene complexes are a common class of organometallic compounds.[6] Other prominent examples of compounds containing transition-metal–lead multiple bonds are the heterocumulenes $[(\eta^5\text{-}C_5H_4R)(CO)_2Mn{=}Pb{=}Mn(CO)_2(\eta^5\text{-}C_5H_4R)]$ (R = H, Me).[7] Two major reasons have emerged from quantum chemical studies for the distinct reluctance of lead to participate in multiple bonding. These are the comparatively low bond energies[8] and the reduced hybridization of its 6s and 6p valence orbitals.[9,10] However, these are not inherent properties of lead, as recently demonstrated by our synthesis of the plumbylidyne complex *trans*-$[Br(PMe_3)_4Mo{\equiv}Pb(2,6\text{-}Trip_2C_6H_3)]$, which features a triply bonded, linear-coordinated lead atom.[11] We have now characterized compounds with tungsten–lead triple bonds. First results of the coordination chemistry of these compounds are also presented, providing experimental evidence for their electronic analogy with Fischer-type carbyne complexes.[12]

Starting materials were the dinitrogen complexes *cis*-$[W(N_2)_2(PMe_3)_4]$ and $[W(N_2)(PMe_3)_5]$[13] and the aryllead(II) halides $[\{Pb(2,6\text{-}Trip_2C_6H_3)X\}_2]$ (X = Br (**1**-Br), I (**1**-I)). Compound **1**-I was prepared by metathetical exchange of **1**-

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Br[14] with NaI in diethyl ether. It was isolated in 82 % yield as an air-sensitive, bright orange solid, which melts at 222 °C and decomposes at 235 °C to give an oily, red mass.[15] Compound **1**-I is the first organolead(II) iodide to be structurally characterized.[16] It crystallizes as a centrosymmetric iodide-bridged dimer, which features a Pb_2I_2 parallelogram with a Pb···Pb separation of 4.603(1) Å[17] and two quite different Pb−I bond lengths (2.9499(7) and 3.2764(8) Å) and internal bond angles (84.81(2) and 95.19(2)°; Figure 1). The Pb−C_{aryl} bond length of **1**-I at 2.326(6) Å compares well with those of **1**-Br (2.306(13) and 2.329(11) Å).[14] Heating a solution of *cis*-$[W(N_2)_2(PMe_3)_4]$ with a stoichiometric amount of **1**-Br or **1**-I in toluene at 100 °C was accompanied by a rapid color change from orange to red-brown to afford the plumbylidyne complex **2**-Br and **2**-I, respectively (Scheme 1).[15,18] Compounds **2**-Br and **2**-I were purified by crystallization from pentane and isolated as red-brown, air-sensitive, microcrystalline solids in 66 (**2**-Br) and 58 % (**2**-I) yields. Both complexes are very soluble in pentane and decompose upon melting at 195 and 192 °C, respectively. The plumbylidyne complex **2**-Br was also obtained in a straightforward manner by the reaction of $[W(N_2)(PMe_3)_5]$ with 0.5 equivalents of **1**-Br in toluene at 100 °C (Scheme 1).[15] This reaction provides another example for the aptitude of electron-rich[19] Group 6 metal dinitrogen complexes with a d^6 electron configuration to form triple bonds to lead. Compounds **2**-Br and **2**-I are essentially isotypic (Figure 2).[15] The isostructural, *trans*-configured octahedral complexes have approximate C_2 point group symmetry,[20] and display almost linear W-Pb-C_{aryl} linkages (**2**-Br, 177.5(2)°; **2**-I, 175.79(8)°) and the shortest W−Pb bonds (**2**-Br, 2.5464(5) Å; **2**-I, 2.5477(3) Å) reported to date.[21] In fact, the W−Pb bond lengths of **2**-Br and **2**-I are 0.20 Å shorter than those of the bridged plumbylidyne complex $[\{W(CO)_4\}_2(\mu\text{-Br})\{\mu\text{-Pb}(2,6\text{-Trip}_2C_6H_3)\}]$ (2.7423(3) and 2.7517(3) Å), which contains a three-coordinate lead center with trigonal-planar geometry,[14] and approximately 0.45 Å shorter than the W−Pb single bonds of the V-shaped tungstenoplumbylene $[Pb(2,6\text{-Trip}_2C_6H_3)\{W(\eta^5\text{-}C_5H_5)(CO)_3\}]$ (2.9809(10) and 3.0055(6) Å).[21d] The Pb−C_{aryl} bonds of **2**-Br (2.254(6) Å) and **2**-I (2.258(3) Å) are shorter than those of **1**-Br and **1**-I (Figure 1), or those reported for the plumbylenes $[Pb(2,6\text{-Trip}_2C_6H_3)R]$ (R = Me, *t*Bu, Ph: Pb−C_{aryl} 2.272(9)–2.321(3) Å)[14] and metalloplumbylenes $[Pb(2,6\text{-Trip}_2C_6H_3)\{M(\eta^5\text{-}C_5H_5)(CO)_3\}]$ (M = Cr, Mo, W: Pb−C_{aryl} 2.278(9)–2.294(4) Å),[21d] and indicate that the triply bonded lead atom uses sp-hybrid orbitals for σ bonding. The composition of **2**-Br and **2**-I was confirmed by elemental analyses and IR, ^1H, $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectroscopy.[15] The number and relative intensity of the ^1H NMR spectroscopy signals of the *m*-terphenyl substituent and the PMe_3 ligands suggest an averaged C_{2v} symmetry of the plumbylidyne complexes **2**-Br and **2**-I in solution, and their $^{31}P\{^1H\}$ NMR spectra in C_6D_6 showed a singlet for the four chemically equivalent PMe_3 ligands, which appears up field (**2**-Br, $\delta =$

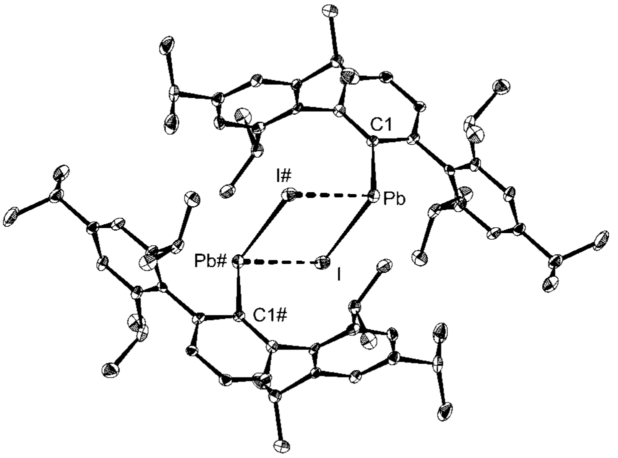
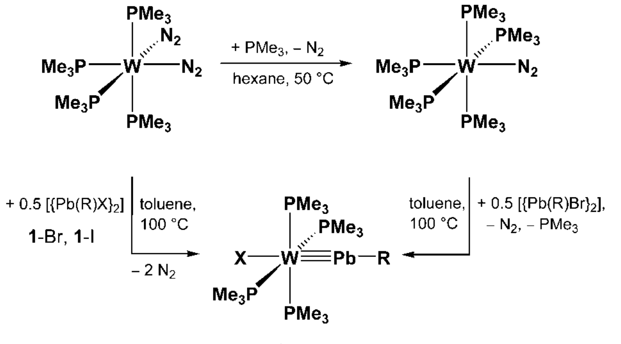


Figure 1. DIAMOND plot of the molecular structure of **1**-I in the solid state. Thermal ellipsoids are set at 30% probability. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Pb-I 2.9499(7), Pb-I# 3.2764(8), Pb-C1 2.326(6); C1-Pb-I 97.3(2), C1-Pb-I# 115.1(2), I-Pb-I# 84.81(2), Pb-I-Pb# 95.19(2).



2-X X = Br, I; R = 2,6-$Trip_2C_6H_3$

Scheme 1. Syntheses of the plumbylidyne complexes **2**-X (X = Br, I).

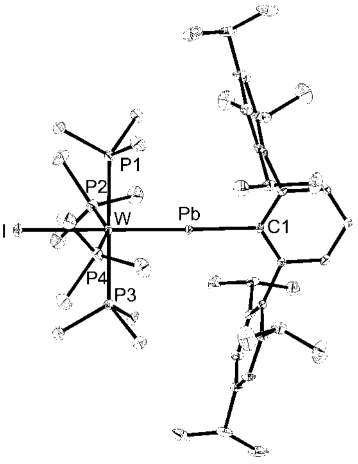
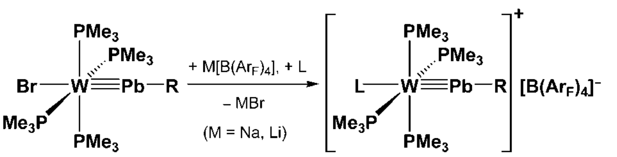


Figure 2. DIAMOND plot of the molecular structure of **2**-I in the solid state. Thermal ellipsoids are set at 30% probability. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°] of **2**-I and [**2**-Br]: W-Pb 2.5477(3) [2.5464(5)], W-I 2.8656(4) [W-Br 2.6798(9)], W-P1 2.4776(9) [2.474(2)], W-P2 2.481(1) [2.484(2)], W-P3 2.4663(9) [2.461(2)], W-P4 2.486(1) [2.485(2)], Pb-C1 2.258(3) [2.254(6)]; W-Pb-C1 175.79(8) [177.5(2)], I-W-Pb 177.857(8) [Br-W-Pb 179.05(3)], Pb-W-P1 90.00(2) [90.17(5)], Pb-W-P2 98.17(2) [100.88(5)], Pb-W-P3 89.01(2) [89.17(4)], Pb-W-P4 102.45(3) [102.84(6)].

−43.6 ppm; **2**-I, $\delta = -53.9$ ppm) of those of the lighter Group 14 element analogues *trans*-$[Cl(PMe_3)_4W{\equiv}E\text{-}R]$ (E = C, R = Me: $\delta_P = -20.8$ ppm, $^1J(W,P) = 285$ Hz;[22] E = Ge, R = C_6H_3-2,6-$Dipp_2$ (Dipp = 2,6-$iPr_2C_6H_3$): $\delta_P = -31.1$ ppm, $^1J(W,P) = 258$ Hz; E = Sn, R = 2,6-$Dipp_2C_6H_3$: $\delta_P = -30.8$ ppm, $^1J(W,P) = 256$ Hz).[23] The ^{31}P NMR signals are flanked by one pair of satellites arising from coupling with the ^{183}W nucleus,[24] the $^1J(W,P)$ coupling constants (**2**-Br, 257 Hz; **2**-I, 258 Hz) comparing well with those of the ylidyne complexes *trans*-$[Cl(PMe_3)_4W{\equiv}E\text{-}R]$ (E = Ge, Sn; R = aryl, see above). The $^{13}C\{^1H\}$ NMR spectra of the plumbylidyne complexes **2**-Br and **2**-I display a characteristic downfield-shifted signal for the lead-bonded C_{ipso} atom at $\delta = 270.2$ (**2**-Br) and 267.9 ppm (**2**-I), as do those of the aryllead(II) halides **1**-Br ($\delta_C = 287.9$ ppm)[14] and **1**-I ($\delta_C = 276.7$ ppm).[15]

Electrophile-induced halide abstraction was shown to be a very efficient method for the preparation of cationic Fischer-type carbyne complexes from neutral precursors.[25] Application of this method to **2**-Br and **2**-I was envisaged as an approach to cationic plumbylidyne complexes, given the electronic analogy of **2**-Br and **2**-I with Fischer-type carbyne complexes.[12] In fact, treatment of **2**-Br with $Na[B\{3,5\text{-}(CF_3)_2C_6H_3\}_4]$[26] and PhCN in toluene afforded the brown benzonitrile complex salt **3**, and bromide abstraction from **2**-Br by $Li[B(C_6F_5)_4]{\cdot}2.5\,Et_2O$[27] in fluorobenzene gave in the presence of PMe_3 the olive-green to brown plumbylidyne complex salt **4** [Eq. (1)].[15] Both salts are soluble in THF, and decompose upon melting at 181–182 (**3**) and 149–150 °C (**4**).



$$Br{-}W(PMe_3)_4{\equiv}Pb{-}R \xrightarrow[\substack{-\,MBr \\ (M = Na,\ Li)}]{+\,M[B(Ar_F)_4],\ +\,L} [L{-}W(PMe_3)_4{\equiv}Pb{-}R]^+[B(Ar_F)_4]^- \qquad (1)$$

2-Br

3, L = PhCN, Ar_F = 3,5-$(CF_3)_2C_6H_3$
4, L = PMe_3, Ar_F = C_6F_5

R = 2,6-$Trip_2C_6H_3$

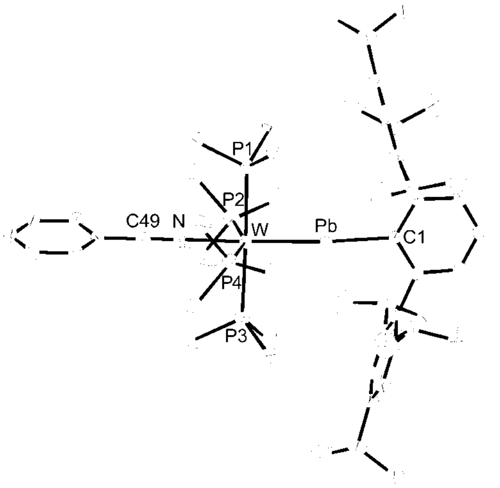


Figure 3. DIAMOND plot of the structure of the complex cation in **3**. Thermal ellipsoids are set at 30% probability. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: W-Pb 2.5520(6), W-N 2.099(4), W-P1 2.469(1), W-P2 2.472(2), W-P3 2.493(2), W-P4 2.496(2), Pb-C1 2.228(5), C49-N 1.137(7); W-Pb-C1 171.7(1), N-W-Pb 174.9(1), Pb-W-P1 90.28(4), Pb-W-P2 95.69(4), Pb-W-P3 91.56(4), Pb-W-P4 104.96(4), W-N-C49 179.1(5).

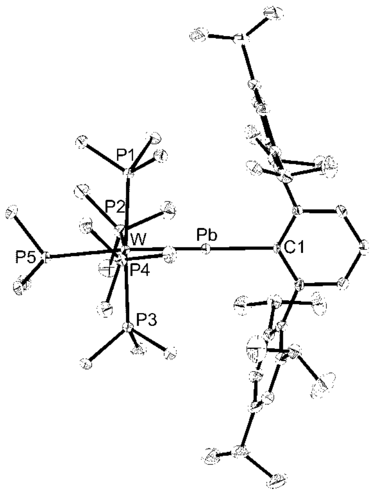


Figure 4. DIAMOND plot of the structure of the complex cation in **4**. Thermal ellipsoids are set at 30% probability. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: W-Pb 2.5744(2), W-P1 2.500(1), W-P2 2.490(1), W-P3 2.513(1), W-P4 2.495(1), W-P5 2.565(1), Pb-C1 2.289(4); W-Pb-C1 177.5(1), Pb-W-P1 87.10(3), Pb-W-P2 93.90(3), Pb-W-P3 88.93 (3), Pb-W-P4 92.93(3), Pb-W-P5 174.87(3).

The structures of the complex cations in **3** and **4** (Figures 3 and 4) reveal the same bonding features of the plumbylidyne ligand as observed in **2**-Br and **2**-I. These are the almost linear coordination geometry at lead (W-Pb-C_{aryl} = 171.7(1) (**3**), 177.5(1)° (**4**)), the short W−Pb triple bonds (2.5520(6) (**3**), 2.5744(2) Å (**4**)), and the comparatively short Pb−C_{aryl} bonds of 2.228(5) Å (**3**) and 2.289(4) Å (**4**). The W−P bond of the *trans*-disposed PMe_3 ligand in **4** is longer (2.565(1) Å) than those of the *cis*-coordinated PMe_3 ligands (2.490(1)–2.513(1) Å), reflecting the *trans*-influence of the plumbylidyne ligand.[28] ^1H, $^{31}P\{^1H\}$, $^{19}F\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectroscopic studies corroborated the X-ray structures of **3** and **4**.[15] Thus, the IR spectrum of **3** in nujol displays a characteristic $\nu(C{\equiv}N)$ band of the benzonitrile ligand at 2171 cm^{-1}, which is at lower wavenumbers than that of free PhCN ($\nu(C{\equiv}N)$ in nujol = 2230 cm^{-1}) and indicates some tungsten–nitrile back-bonding.[29] In addition, the $^{31}P\{^1H\}$ NMR spectrum of **3** shows a singlet resonance at $\delta = -36.8$ ppm ($^1J(W,P) = 262$ Hz) for the PMe_3 ligands, which confirms the *trans*-configuration of the complex cation in **3**. In comparison, the $^{31}P\{^1H\}$ NMR spectrum of **4** reveals the signal pattern expected for a nonfluxional, square-pyramidal $W(PMe_3)_5$ fragment, that is, one doublet at $\delta = -52.1$ ppm ($^2J(P,P) = 31$ Hz, $^1J(W,P) = 249$ Hz) and one quintet at $\delta = -65.6$ ppm ($^2J(P,P) = 31$ Hz) in the intensity ratio of 4:1.[15] The structures of **3** and **4** are also confirmed by the Pb-C_{ipso} resonance signal in the $^{13}C\{^1H\}$ NMR spectra at $\delta = 278.7$ (**3**) and 279.1 ppm (**4**). The C_{ipso} signal of **4** is split into a doublet as a result of coupling with the *trans*-disposed PMe_3 ligand ($^3J(P,C) = 22$ Hz).

The similarity of the plumbylidyne complex $[(PMe_3)_5W{\equiv}Pb(2,6\text{-}Trip_2C_6H_3)]^+$ with the Fischer-type carbyne complexes

Table 1: Results of the bonding analyses of the cation of **4**.

		NBO analysis[a]						BDE[c]	EDA[d] [kJmol^{-1}]			
center	NPA[b] charges	occupancy	%(W)	hybrid.	%(Pb)	hybrid.	WBI	[kJmol^{-1}]	$\Delta E_{\mathrm{Pauli}}$	$\Delta E_{\mathrm{elstat}}$	ΔE_{orb}	ΔE_{int}
W	−1.58	σ: 1.71	41.1	sd$^{1.54}$	58.9	sp$^{0.77}$	1.42	149.7	+472.0	−352.0	−530.9	−410.9
Pb	+1.21	π_1:1.85	81.0	d	19.0	p						
		π_2: 1.83	81.0	d	19.0	p						

[a] BP86/LANL2DZ; Natural bond orbital analysis of the W−Pb bond: NBO occupancies, bond polarization in % W and % Pb, orbital hydridization, and Wiberg bond index. [b] Natural population analysis. [c] Gibbs free dissociation energy (298.15 K, 1 atm) of the W−Pb bond to the fragments in their relaxed geometries and electronic ground states (zero point energy (ZPE) corrected). [d] Energy decomposition analysis (BP86/TZ2P for Pb, W, and P, and DZP for C and H): Pauli repulsion ($\Delta E_{\mathrm{Pauli}}$), electrostatic interaction ($\Delta E_{\mathrm{elstat}}$), orbital interaction ($\Delta E_{\mathrm{orb}}$), and total interaction energy ΔE_{int} between the fragments [W(PMe$_3$)$_5$] and [Pb(2,6-Trip$_2$C$_6$H$_3$)]$^+$ at their frozen geometries in the complex cation.

$[(CO)_5M{\equiv}C\text{-}NEt_2]^+$ (M = Cr, Mo, W) is noticeable.[30] This fact prompted us to study the nature of the W−Pb bond in **4** by various quantum chemical methods. Optimization of the structure of the complex cation at the BP86/LANL2DZ level of theory led to a minimum structure with a W−Pb separation of 2.609 Å and a bond angle at the lead atom of 174.9° in good agreement with the experimental values (Figure 4). Analysis of the electronic charge distribution by the natural bond orbital (NBO) method[31] gives an optimal Lewis structure with a W−Pb triple bond. The W−Pb bond is composed of a σ component that is polarized towards the lead atom, and two nearly degenerate π bonds, which are strongly polarized towards the tungsten center (Table 1). The high polarity of the W−Pb bond is further reflected in the natural population analysis (NPA) partial charges of the Pb (+1.21) and W atom (−1.58) and the Wiberg bond index (WBI) of 1.42 (Table 1), which is slightly lower than that of the model compound *trans*-[Br(PH$_3$)$_4$Mo≡Pb-Ph] (WBI = 1.51).[11] Partitioning of the total interaction energy ΔE_{int} (−410.9 kJ mol^{-1}) between the frozen fragments [W(PMe$_3$)$_5$] and [Pb(2,6-Trip$_2$C$_6$H$_3$)]$^+$ into the attractive Coulomb term $\Delta E_{\mathrm{elstat}}$ of −352.0 kJ mol^{-1}, the repulsive Pauli term $\Delta E_{\mathrm{Pauli}}$ of +472.0 kJ mol^{-1}, and the orbital interaction term ΔE_{orb} of −530.9 kJ mol^{-1} affords a covalent character of 60 % for the W≡Pb bond.[32] All these results suggest that the W−Pb triple bond of **4** can be reasonably described with the Dewar–Chatt–Duncanson model as a donor–acceptor interaction involving a $[PbR]^+ \rightarrow [W(PMe_3)_5]$ σ donation and two $[W(PMe_3)_5] \rightarrow [PbR]^+$ π back-donations.[33]

Finally, the Gibbs free dissociation energy of **4** to give the fragments [W(PMe$_3$)$_5$] and [Pb(2,6-Trip$_2$C$_6$H$_3$)]$^+$ in their electronic ground states and minimum geometries[34,35] was calculated to be only 149.7 kJ mol^{-1}, which suggests that the complex cation might be useful as a [Pb-R]$^+$ transfer reagent.

Several applications of these compounds in stoichiometric reactions might be envisaged given their structural and electronic analogy with Fischer-type carbyne complexes.

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