

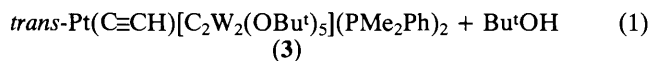
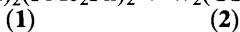
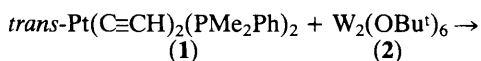
Synthesis, X-Ray Crystal Structure, and N.M.R. Studies of *trans*-Bis(dimethylphenylphosphine)bis[$\{\text{dicarbido}(4-)\sigma\text{-Pt}, \sigma\text{-W}^1, \eta^2\text{-W}^2\}$]-pentakis(*t*-butoxy)ditungsten($M=M$)]platinum(II)

Reed J. Blau, Malcolm H. Chisholm,* Kirsten Folting, and Ruji J. Wang

Department of Chemistry and Molecular Structure Center, Indiana University, Bloomington, IN 47405, U.S.A.

In hydrocarbon solutions *trans*-Pt(C≡CH)₂(PMe₂Ph)₂, (1), and W₂(OBU^t)₆, (2), react to give, by successive eliminations of Bu^tOH, *trans*-Pt(C≡CH)[C₂W₂(OBU^t)₅](PMe₂Ph)₂, (3), and *trans*-Pt[C₂W₂(OBU^t)₅]₂(PMe₂Ph)₂, (4); compounds (3) and (4) are shown to contain dicarbido(4-) ligands on the basis of ¹³C n.m.r. studies and single crystal X-ray crystallography.

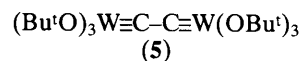
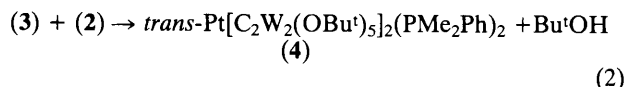
The reactions between W₂(OR)₆ (M≡M) compounds and alkynes have yielded a variety of products including terminal¹⁻⁴ and bridging (μ₂^{5,6} and μ₃^{7,8}) alkylidyne complexes, alkyne adducts,⁹ and μ-C₄R'₄ containing compounds.^{10,11} We anticipated that reactions employing metal-alkynyl complexes would provide an entry into heterometallic carbido chemistry^{12,13} in which the tungsten(s) and heterometal atom(s) would be co-ordinated to either a C⁴⁻ or C₂^{x-} unit (x = 2, 3, 4, 5, or 6). We describe here some pertinent observations of the reaction between *trans*-Pt(C≡CH)₂(PMe₂Ph)₂, (1), and W₂(OBU^t)₆, (2), which proceeds according to equation (1).



This reaction has been monitored by ¹H, ¹³C, and ³¹P n.m.r. spectroscopy. Dry and oxygen-free atmospheres (N₂) and solvents were used. We have also followed the reaction between the ¹³C labelled ethynyl compound, *trans*-Pt(¹³C≡*CH)₂(PMe₂Ph)₂, (1*), which exists in a variety of isotopomers resulting from its preparation employing commercially available (Merk, Sharp, and Dohme) H^{*}C≡CH, where *C represents 92% g atom ¹³C. In these reactions the labelled ¹³C compounds (3*) and (4*) are formed.

When reaction (2) is carried out in benzene at 30 °C, formation of (4) is essentially complete within 4–5 days. Compound (3) is only sparingly soluble in hexane but appreciably soluble in benzene and toluene whereas compound (4) is very soluble in all three solvents. This has allowed separation of (3) and (4) by fractional crystallization.

The molecular structure of (4) is centrosymmetric and a ball and stick view of the pertinent centrosymmetric PtP₂(C₂W₂O₅)₂ skeleton is shown in Figure 1.† The central



PtP₂C₂ unit is essentially square planar and the bond distances and coupling constants to ¹⁹⁵Pt establish this as formally Pt²⁺. The C₂W₂ unit is planar and this plane is roughly perpendicular to the PtP₂C₂ plane. The Pt(1)–C(4) and W(3)–C(5)

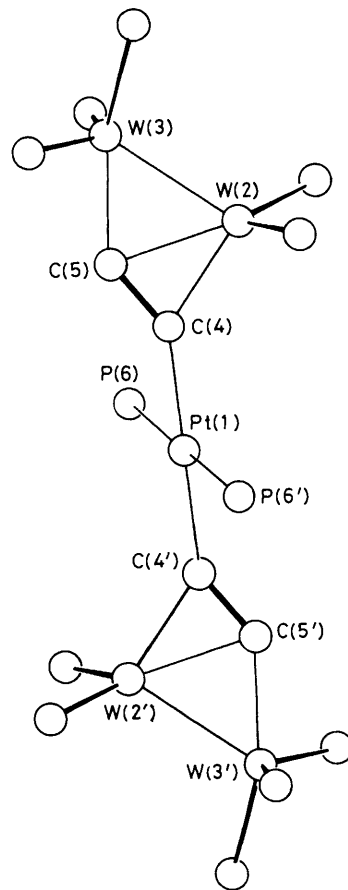


Figure 1. A ball and stick view of the central *trans*-PtP₂(C₂W₂O₅)₂ moiety of the centrosymmetric *trans*-Pt(PMe₂Ph)₂{C₂W₂(OBU^t)₅}₂ molecule looking nearly down the P–Pt–P axis showing the planar PtC₂W₂ unit. Selected bond distances (Å) and angles (°) are: Pt–C(4) 2.06(1), Pt–P 2.29(1), W–W 2.44(1), W(2)–C(4) 2.05(1), W(2)–C(5) 2.12(1), W(3)–C(5) 2.06(1), W–O 1.91(2) (averaged), C(4)–C(5) 1.33(1), Pt–C(4)–C(5) 144.0(1), Pt–C(4)–W(2) 140.5(1), W(2)–C(4)–C(5) 74.4(1), W(3)–C(5)–C(4) 140.2(1), W(2)–C(5)–C(4) 68.6(1), W(2)–C(5)–W(3) 71.7(1).

† Crystal data for *trans*-Pt[W₂C₂(OBU^t)₅]₂(PMe₂Ph)₂·hexane at –155 °C: *a* = 11.983(5), *b* = 17.413(10), *c* = 10.574(5) Å, α = 92.31(3), β = 107.87(2), γ = 108.59(2)°, *Z* = 1, space group *P*1. The Pt, W, P, O, and C atoms were refined anisotropically; hydrogen atoms were included in fixed calculated positions. Of the 5162 unique intensities collected using Mo-*K*_α, 6° ≤ 2θ ≤ 45°, the 4544 having *F* > 2.33 σ(*F*) were used in the full least squares refinement. The present level of refinement is *R*(*F*) = 0.035 and *R*_w(*F*) = 0.036.

The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

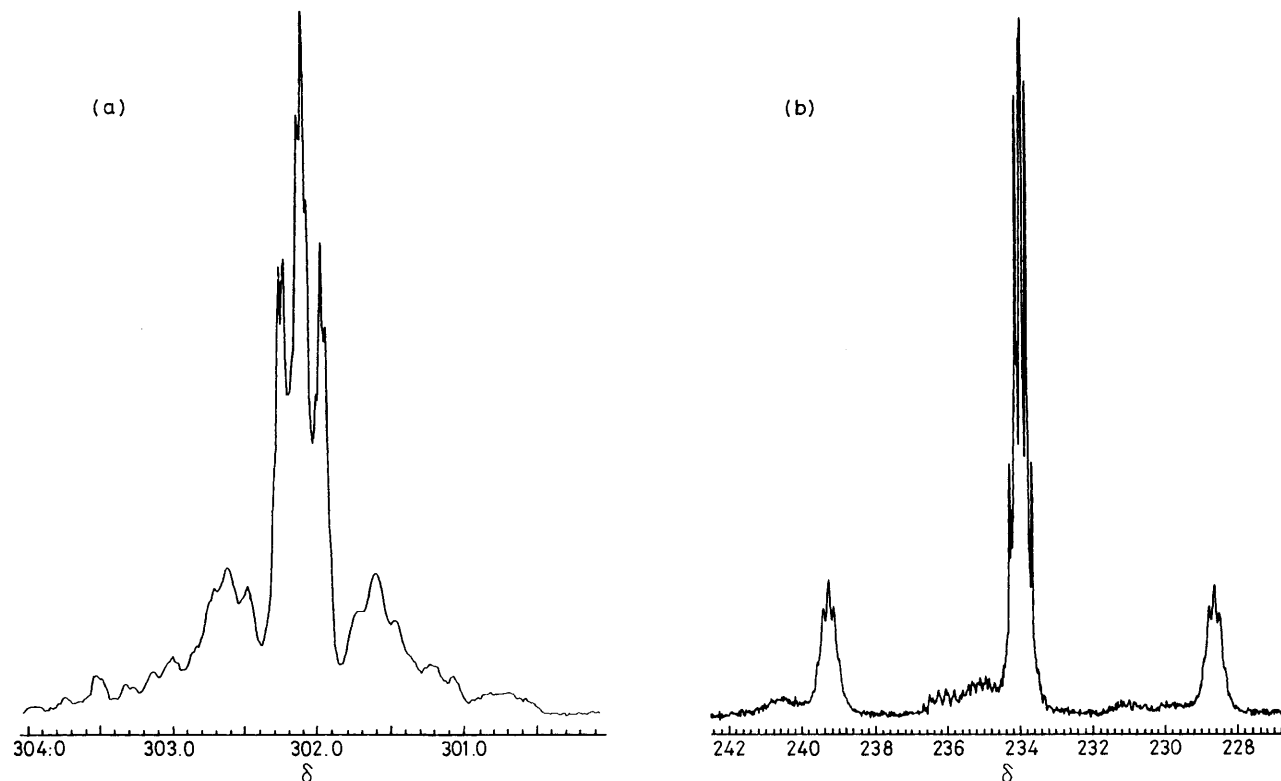


Figure 2. Part of the ^{13}C n.m.r. spectrum of (**4***); (a) C(5) and (b) C(4) resonances. The spectrum was obtained using a Varian XL-300 instrument at 75 MHz. The central resonances, characteristic of an AA'LL'XX' [C(4)C(4')C(5)C(5')PP'] coupled system, are skirted by both ^{195}Pt ($I = 1/2$, 33.7% natural abundance) and ^{183}W ($I = 1/2$, 14.3% natural abundance) satellites. The central resonances can be reasonably simulated using the coupling constants quoted in footnote§.

distances may be taken to represent single bond distances and the C(4)–C(5) distance, 1.33(1) Å, and W(2)–W(3) distance, 2.445(1) Å, as C–C¹⁶ and W–W¹⁷ double bond distances, respectively. This allows the formal electron counting of the C₂ unit as C₂⁴⁻. The W₂(C₂–Pt) moiety is reminiscent of the Mo₂(NC–N) moiety in Mo₂(OCH₂Bu^t)₆(μ–NCNMe₂)¹⁸ which, by a similar electron counting scheme, may be viewed as (Mo=Mo)⁸⁺ and Me₂NC=N²⁻.

Compound (**3**), though not structurally characterized, is unequivocally characterized by the n.m.r. spectroscopic detection of the PtC₂W₂(OBu^t)₅ and PtC≡CH moieties.‡ The

^{13}C n.m.r. spectra of the labelled compounds (**3***) and (**4***) are particularly informative though extremely complex due to the complex spin systems and the presence of several isotopomers. The ^{13}C n.m.r. spectrum of the Pt* C₂W₂ carbons in (**4***) is shown in Figure 2. The C(4) resonance at δ ca. 233 shows, as expected, the largest coupling to ^{195}Pt , $^1J(^{195}\text{Pt}-^{13}\text{C})$ 801 Hz, while the C(5) resonance at δ 302 shows the largest coupling to ^{183}W , $^1J(^{183}\text{W}-^{13}\text{C})$ 133 Hz, presumably involving W(3). The ^{13}C – ^{13}C coupling in the C₂⁴⁻ ligand is ca. 18 Hz, greatly reduced from 172 Hz in free ethyne^{19,20} and 122 Hz in the Pt–C≡CH moiety in (**1***) and (**3***). The low value of $J(^{13}\text{C}-^{13}\text{C})$ in the PtC₂W₂ moiety is similar to the values seen for W₂(μ–C₂R₂)-containing compounds supported by alkoxide ligands where the central W₂C₂ unit is best described as a dimetallatetrahedrane.¹¹

A minor compound formed in the reaction between (**1**) and (**2**) is (Bu^tO)₃W≡C–C≡W(OBu^t)₃,² (**5**), which in the ^{13}C labelled isotopomers, (**5***), reveals: $^1J(^{183}\text{W}-^{13}\text{C})$ 300.3, $^2J(^{183}\text{W}-^{13}\text{C})$ 54.7, and $^1J(^{13}\text{C}-^{13}\text{C})$ 44.5 Hz.

To our knowledge, no other co-ordination complexes containing the C₂⁴⁻ ligand have been reported. Its mode of bonding is very similar to the acetylide unit in Fe₂(CO)₆–(μ₂–η²–C≡CPh)(μ₂–PPh₂)²¹ and those in other related^{22,23} binuclear acetylides, M₂(CO)₄(L)₂(η²–μ₂–C≡CR)(μ₂–PPh₂), where M = Fe, Ru and R = alkyl, aryl. However, the C–C bond distances in these acetylides are considerably shorter (1.22–1.23 Å)^{21–23} than those in (**4**) (1.33 Å). There are also

‡ Selected n.m.r. data based on satisfactory simulation of the spectra for (**1***), (**3***), and (**4***) in [C₆H₆]benzene.

(**1***): for HC≡C–Pt–C≡CH ^{13}C n.m.r.: δ 100.71 [C_α, $^1J(^{195}\text{Pt}-^{13}\text{C})$ 947.9, $^2J(^{31}\text{P}-^{13}\text{C})$ 15.0 Hz], 94.87 [C_β, $^1J(^{195}\text{Pt}-^{13}\text{C})$ 265.7, $^1J(^{13}\text{C}_\alpha-^{13}\text{C}_\beta)$ 121.9, $^3J(^{13}\text{C}_\alpha-^{13}\text{C}_\beta)$ 10.5, $^2J(^{13}\text{C}_\alpha-^{13}\text{C}_\alpha')$ 40 Hz].

(**3**): ^1H n.m.r.: δ 2.40 [≡CH, $^3J(^{195}\text{Pt}-^1\text{H})$ 43, $^2J + ^4J(^{31}\text{P}-^1\text{H})$ 4.3 Hz], 1.79 [PMe, $^3J(^{195}\text{Pt}-^1\text{H})$ 32, $^2J + ^4J(^{31}\text{P}-^1\text{H})$ 7.2 Hz], 1.56 (OBu^t, 2H), 1.53 (OBu^t, 3H), 7.9 (phenyl-*o*-H); ^{31}P n.m.r. δ –11.2 p.p.m. [PMe₂Ph, $^1J(^{195}\text{Pt}-^{31}\text{P})$ 2591 Hz]; ^{13}C n.m.r. data for HC≡C–Pt–C≡C₂: δ 100.5 [C_α, $^1J(^{195}\text{Pt}-^{13}\text{C})$ 941, $^2J(^{31}\text{P}-^{13}\text{C}_\alpha)$ 16.0 Hz], 97.12 [C_β, $^2J(^{195}\text{Pt}-^{13}\text{C}_\beta)$ 259.4 Hz], 235.16 [C₁, $^1J(^{195}\text{Pt}-^{13}\text{C}_1)$ 802, $^2J(^{31}\text{P}-^{13}\text{C}_1)$ 11.5 Hz], 302.1 [C₂, $^1J(^{195}\text{Pt}-^{13}\text{C}_2)$ 78.2, $^1J(^{183}\text{W}-^{13}\text{C}_2)$ 132, $^3J(^{31}\text{P}-^{13}\text{C}_2)$ 2 Hz].

(**3***): $^1J(^{13}\text{C}_\alpha-^{13}\text{C}_\beta)$ 122.2, $^2J(^{13}\text{C}_\alpha-^{13}\text{C}_1)$ 36.2, $^3J(^{13}\text{C}_\alpha-^{13}\text{C}_2)$ 3.3, $^3J(\text{C}_1-\text{C}_\beta)$ 12.0, $^1J(\text{C}_1-\text{C}_2)$ 18.5 Hz.

(**4**): ^1H n.m.r. δ 1.77 [PMe, $^3J(^{195}\text{Pt}-^1\text{H})$ 30, $^2J + ^4J(^{31}\text{P}-^1\text{H})$ 69 Hz], 1.51 (OBu^t, 2H), 1.48 (OBu^t, 3H), 8.01 (phenyl *o*-H); ^{31}P n.m.r.: δ –8.0 p.p.m. [PMe₂Ph, $^1J(^{195}\text{Pt}-^{31}\text{P})$ 2776 Hz]; ^{13}C n.m.r. for C(5')=C(4')–Pt–C(4)=C(5): δ 233.9 [C(4), $^1J\{^{195}\text{Pt}-^{13}\text{C}(4)\}$ 801, $^1J\{^{183}\text{W}-^{13}\text{C}(4)\}$ 50.5, $^2J\{^{31}\text{P}-^{13}\text{C}(4)\}$ 12.5 Hz], 302.0 [C(5), $^2J\{^{195}\text{Pt}-^{13}\text{C}(5)\}$ 76.3, $^1J\{^{183}\text{W}-^{13}\text{C}(5)\}$ 132.7, $^1J\{^{183}\text{W}-^{13}\text{C}(5)\}$ 19.5, $^3J\{^{31}\text{P}-^{13}\text{C}(5)\}$ 2.2 Hz].

§ (**4***) AA'LL'XX' pattern where $N = ^1J + ^3J\{^{13}\text{C}(4)-^{13}\text{C}(5)\}$ 21.6 Hz. Reasonable simulation of the central resonances shown in Figure 2 may be obtained for $^1J\{^{13}\text{C}(4)-^{13}\text{C}(5)\} = 18.5$, $^3J\{^{13}\text{C}(4)-^{13}\text{C}(5')\} = 3.1$, $^2J\{^{13}\text{C}(4)-^{13}\text{C}(4')\} = 39.4$ Hz.

pronounced differences (>100 p.p.m.) in the chemical shifts of the respective C_2^{n-} carbon atoms. Those of the iron and ruthenium acetylides range between δ 90 and 110.²²

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