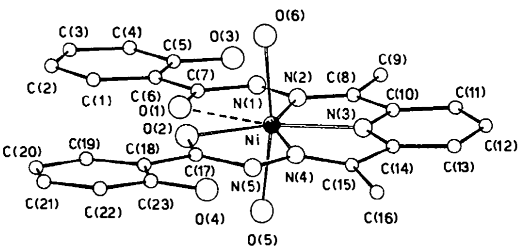

Fig. 1. A perspective view of the $[Ni(H_2daps)(OH_2)_2]^{2+}$ cation.

structure of two previously reported pentagonal-bipyramidal Ni^{II} cations, namely diaqua[2,6-diacetylpyridine bis(semicarbazone)]nickel (Wester & Palenik, 1974) and diaqua[2,6-diacetylpyridine bis(benzoic acid hydrazone)]nickel (Giordano, Palenik, Palenik & Sullivan, 1979). In this compound, H_2daps encircles the Ni^{II} ion in an unsymmetrical quinquedentate fashion, this being mainly associated with the non-equivalence of the two Ni—O bonds, which are notably different at 2·628 (6) and 2·247 (6) Å. This disparity, which explains the splitting of the CO frequency value observed in the infrared spectrum, has already been observed, even if to a lesser extent, in both the aforementioned compounds and has been attributed to Jahn–Teller distortions. It can be added that in our compound only the O atom that is bonded more weakly to Ni is involved in an intermolecular hydrogen bond with a water molecule.

The five interior angles in the pentagon range from 65·7 (2) to 76·0 (3)° with an average of 72°, which is the expected value for an idealized pentagon. The N_3O_2 donor set of atoms that forms the pentagon is not completely planar, with maximum atom deviations of 0·09 Å. The angle between the apical ligands is 168·8 (3)° and those between apical and equatorial atoms are close to 90°, their range being 81·8 (2)–96·2 (3)°.

The molecule contains two intramolecular hydrogen bonds which occur between the hydrazidic N atoms, N(1) and N(5), and the hydroxyl O atoms, O(3) and O(4) [N(1)···O(3) 2·58 (1); N(5)···O(4) 2·62 (1) Å]. As regards the crystal packing, the structure is stabilized by an extensive network of hydrogen bonds, which involve the complex cations, through the hydroxyl and the water O atoms, the nitrate anions and the uncoordinated water molecules.

In summary, from this and the preceding studies of 2,6-diacetylpyridine bis(acylhydrazones) it appears that, among the different conformations the ligand can assume in coordinating to metal ions, the quinquedentate planar conformation is the favoured one.

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Reactions of Coordinated Molecules. 48. The Structure of a Pt–W Cluster Containing a Bridging η^1,η^3-*p*-Tolylmethylene Ligand

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Abstract. μ-Carbonyl-2-carbonyl-2-η-cyclopentadienyl-μ-[σ:η^3-*p*-tolylmethylene-C^{α}(Pt,W)$C^{1,2}$(W)]-1,1-bis(triethylphosphine)platinumtungsten(1+)(*Pt–W*) tetrafluoroborate, $[(\eta\text{-}C_5H_5)(OC)_2W\{\mu\text{-}\eta^1,\eta^3\text{-}C(C_6H_4\text{-}CH_3\text{-}p)(H)\}Pt\{P(CH_2CH_3)_3\}_2]BF_4$: $M_r = 927{\cdot}33$, orthorhombic, $Pca2_1$, $a = 18{\cdot}240\ (4)$, $b = 11{\cdot}231\ (3)$, $c = 15{\cdot}817\ (4)$ Å, $V = 3240$ Å^3, $Z = 4$, $D_x = 1{\cdot}901$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu =$

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81·24 cm^{-1}, $F(000) = 1776$, $T = 294$ K, final R value is 0·068 for 2971 measured reflections. The Pt—W distance of 2·797 (1) Å represents a normal single-bond length. The metal atoms are connected by an asymmetrically bridging carbonyl ligand and by a bridging C(*p*-tolyl)(H) alkylidene ligand. The *ortho* C—C bond of the *p*-tolyl group is also coordinated to the W atom. This rather unusual η^1,η^3-alkylidene coordination mode enables the W atom to obey the EAN (effective atomic number) rule.

Introduction. We reported recently that the Pt—H bond of the cationic complex $[trans\text{-}Pt(H)(PEt_3)_2\text{-}(acetone)]BF_4$ adds across the C≡C triple bond of one of the phenyl acetylide ligands of *trans*-$Pt(PEt_3)_2(C{\equiv}CPh)_2$ or the W≡C triple bond of the carbyne complex, $(\eta\text{-}C_5H_5)(OC)_2W{\equiv}CC_6H_4CH_3\text{-}p$, to give, respectively, a cationic diplatinum cluster containing a bridging phenyl vinylidene ligand (Afzal, Lenhert & Lukehart, 1984) or a cationic Pt—W cluster containing a bridging alkylidene ligand (Davis & Lukehart, 1984). The X-ray structure of the cationic diplatinum cluster is included in the original report. We present herein the X-ray structure of the cationic Pt—W cluster, $[(\eta\text{-}C_5H_5)(OC)_2W\{\mu\text{-}\eta^1,\eta^3\text{-}C(C_6H_4CH_3\text{-}p)(H)\}Pt(PEt_3)_2]BF_4$, to confirm unambiguously the identity of the cluster formed by the formal addition of a Pt—H bond to a carbyne complex. The cation contains a W—Pt single bond, an asymmetrically bridging carbonyl ligand, and a bridging η^1,η^3-C(*p*-tolyl)(H) alkylidene ligand. The structure of an analogous complex (though prepared *via* a different method) has been reported recently (Jeffrey, Laurie, Moore, Razay & Stone, 1984).

Experimental. The complex was prepared (Davis & Lukehart, 1984) and crystallized as amber needles from THF/pentane at 253 K. Laue symmetry (*mmm*), absent reflections (l odd for $0kl$ and h odd for $h0l$) and expected density require the space group $Pca2_1$. Reported cell parameters are from a least-squares fit of 2θ, ω, χ for 11 reflections ($30 < 2\theta < 40°$) measured at both $\pm 2\theta$ with unresolved Mo $K\alpha$ (0·71070 Å).

A crystal 0·4 × 0·2 × 0·2 mm was mounted with the large dimension parallel to the diffractometer φ axis for intensity measurement. The Picker FAC-I software (Lenhert, 1975) was used to measure 2θ step scans to $\sin\theta/\lambda$ of 0·5947 Å^{-1} with Mo $K\alpha$ from a graphite monochromator. For the 6687 reflections ($\pm h \pm kl$, 0–20° 2θ; hkl and $-h-k-l$, 20–50° 2θ) measurement conditions were: 2θ steps, 0·05°; scan width 1·15° plus dispersion; background for 20 s at scan ends. Five monitor reflections were measured at intervals. Each interval was scaled to correct for the intensity decrease which accumulated to 16%. Absorption was corrected with *ORABS* (Wehe, Busing & Levy, 1962) using an 8 × 8 × 8 Gaussian grid. Maximum, minimum and average transmission factors were 0·425, 0·334 and 0·396. Equivalent reflections were averaged to give 2971 F_o, all (including 156 with zero intensity) were used for refinement.

A sharpened Patterson function gave W and Pt coordinates. A difference synthesis located all other atoms except H, which were calculated. For the final full-matrix least-squares refinement non-H atoms were anisotropic (isotropic H atoms were included but not refined). The quantity minimized was $\sum w(|F_o| - |F_c|)^2$, where $w = 1/\sigma(F_o)^2$. The variance, σ^2, based on counting statistics included an instability term (4·0%). Heavy-atom scattering factors were from Cromer & Mann (1968), anomalous-dispersion factors from Cromer & Liberman (1970); and H-atom scattering factors from Stewart, Davidson & Simpson (1965). The final R was 0·064, $wR = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, was 0·045 for all reflections. The maximum shift to e.s.d. ratio for the final refinement cycle was 0·19, the standard e.s.d. of an observation of unit weight 1·9, maximum and minimum $\Delta\rho$ values were 1·12 e Å^{-3} (near Pt) and $-1·32$ e Å^{-3}. (Refinement with the mirror-image molecule did not give a significantly different value for R.)

Structure factor, electron density, and bond distance and angle calculations were performed with the *XRAY*67 (Stewart, 1967) programs as implemented and updated on the Vanderbilt DEC10 computer.

Discussion. Atomic parameters are given in Table 1, selected interatomic distances and angles in Table 2.* An *ORTEP* view of the molecular structure including the atomic numbering scheme is shown in Fig. 1.

The Pt—W distance of 2·797 (1) Å represents a metal–metal single-bond length. The Pt atom has unusual coordination geometry overall, though two of the five ligands form a more frequently observed 'Y-shaped' PtP_2 fragment having a P(1)—Pt—P(2) angle of 98·4 (2)°. The Pt atom is also coordinated to a bridging carbonyl ligand and a bridging alkylidene ligand. The W atom is coordinated to an η-C_5H_5 ligand, a terminal carbonyl ligand, C(2)O(2), the bridging CO and alkylidene ligands, and to the *ortho* C(41)—C(42) bond of the *p*-tolyl group (in addition to being bonded to the Pt atom). This coordination gometry satisfies the EAN rule at W. The Pt moiety is formally a 16-electron complex.

The W—C_5H_5 (plane) distance is 1·965 Å. The terminal carbonyl ligand has a W—C(2) distance of

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* Lists of final atomic positional and thermal parameters before rounding, additional bond distances and angles, selected least-squares planes and dihedral angle data, and final observed and calculated structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42952 (23 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

1·95 (3) Å and a W—C(2)—O(2) angle of 170 (2)°. The asymmetrically bridging carbonyl ligand is characterized by the unequal W—C(1) and Pt—C(1) distances of 1·99 (3) and 2·23 (3) Å, respectively.

Table 1. *Final fractional positional coordinates* (×10⁴) *and equivalent isotropic temperature factors* (Å²)

$B_{eq} = \frac{8}{3}\pi^2(U_{11}^2 + U_{22}^2 + U_{33}^2)$, where the U_{ii} are the principal r.m.s. vibration amplitudes in Å.

	x	y	z	B_{eq}
Pt	5599·4 (4)	3397·4 (6)	1814·0	3·04
W	4443·0 (4)	1803·2 (6)	1554·2 (6)	3·30
P(1)	5516 (3)	5315 (5)	1301 (4)	3·73
P(2)	6716 (3)	3566 (5)	2499 (4)	3·82
F(1)	1336 (11)	1544 (17)	3276 (13)	12·44
F(2)	1271 (10)	1011 (14)	1963 (16)	12·68
F(3)	2112 (8)	2229 (11)	2392 (12)	9·99
F(4)	2159 (7)	319 (11)	2766 (12)	9·36
O(1)	5278 (10)	2825 (14)	21 (11)	6·30
O(2)	3375 (9)	3998 (13)	1520 (14)	8·65
B	1763 (20)	1259 (29)	2627 (26)	6·77
C(1)	5042 (11)	2629 (17)	684 (14)	3·87
C(2)	3839 (13)	3233 (18)	1511 (17)	5·93
C(11)	6347 (13)	5874 (17)	757 (15)	5·10
C(12)	6558 (15)	5188 (21)	−17 (15)	5·85
C(13)	5287 (11)	6426 (16)	2126 (14)	4·40
C(14)	4618 (14)	6195 (26)	2682 (20)	8·51
C(15)	4784 (11)	5562 (21)	536 (15)	5·62
C(16)	4663 (13)	6835 (18)	210 (15)	5·62
C(21)	6965 (10)	4945 (19)	3047 (14)	5·21
C(22)	6482 (16)	5230 (23)	3833 (15)	6·57
C(23)	6932 (10)	2405 (16)	3300 (13)	4·24
C(24)	7675 (13)	2438 (18)	3692 (16)	6·28
C(25)	7438 (9)	3250 (17)	1721 (13)	5·21
C(26)	7386 (12)	2124 (18)	1170 (17)	6·10
C(31)	3864 (17)	856 (23)	501 (14)	5·95
C(32)	3402 (13)	751 (22)	1178 (19)	6·18
C(33)	3735 (11)	93 (16)	1831 (14)	4·44
C(34)	4425 (13)	−263 (15)	1524 (16)	5·05
C(35)	4481 (14)	149 (24)	761 (18)	6·41
C(40)	5447 (8)	1798 (15)	2352 (12)	3·23
C(41)	4937 (11)	1565 (16)	2976 (16)	4·26
C(42)	4394 (13)	2414 (17)	3113 (15)	4·62
C(43)	3790 (13)	2136 (21)	3670 (16)	5·82
C(44)	3669 (16)	1100 (26)	4105 (18)	6·80
C(45)	4216 (15)	254 (23)	3965 (14)	5·93
C(46)	4829 (11)	432 (18)	3465 (14)	4·57
C(47)	3014 (14)	839 (23)	4726 (18)	8·14

Table 2. *Selected interatomic distances* (Å) *and angles* (°)

Pt—W	2·797 (1)	W—C(41)	2·44 (3)
Pt—P(1)	2·306 (5)	W—C(42)	2·56 (3)
Pt—P(2)	2·313 (5)	P(1)—C(11)	1·85 (3)
Pt—C(1)	2·23 (3)	P(1)—C(13)	1·85 (2)
Pt—C(40)	2·01 (2)	P(1)—C(15)	1·82 (3)
W—C(1)	1·99 (3)	P(2)—C(21)	1·83 (3)
W—C(2)	1·95 (3)	P(2)—C(23)	1·86 (2)
W—C(31)	2·24 (3)	P(2)—C(25)	1·84 (2)
W—C(32)	2·32 (3)	C(1)—O(1)	1·16 (3)
W—C(33)	2·35 (2)	C(2)—O(2)	1·21 (3)
W—C(34)	2·32 (2)	C(40)—C(41)	1·38 (3)
W—C(35)	2·24 (3)	C(41)—C(42)	1·39 (3)
W—C(40)	2·22 (2)	C(41)—C(46)	1·50 (3)
W—Pt—C(1)	44·8 (6)	Pt—P(2)—C(23)	116·6 (7)
W—Pt—C(40)	52·0 (5)	Pt—P(2)—C(25)	107·6 (7)
W—Pt—P(1)	119·8 (2)	Pt—C(1)—O(1)	119 (2)
W—Pt—P(2)	141·7 (2)	Pt—C(40)—C(41)	125 (2)
Pt—W—C(1)	52·3 (6)	W—C(1)—O(1)	157 (2)
Pt—W—C(2)	84·5 (7)	W—C(2)—O(2)	170 (2)
Pt—W—C(40)	45·4 (5)	P(1)—Pt—P(2)	98·4 (2)
Pt—P(1)—C(11)	115·3 (7)	C(40)—C(41)—C(42)	118 (2)
Pt—P(1)—C(13)	113·3 (7)	C(40)—C(41)—C(46)	128 (2)
Pt—P(1)—C(15)	115·1 (8)	C(41)—C(42)—C(43)	119 (2)
Pt—P(2)—C(21)	120·7 (7)	C(42)—C(41)—C(46)	114 (2)

The bridging alkylidene donor atom C(40) has pyramidal hybridization [the sum of the three angles centered at C(40) is 288·6°], and has an H atom substituent, also. In addition, atoms C(41) and C(42) are bonded to the W atom because of the η^2-arene coordination. The W—C(40), W—C(41) and W—C(42) distances are 2·22 (2), 2·44 (3) and 2·56 (3) Å, respectively. The corresponding distances in an analogous compound containing PMe_3 ligands are, respectively, 2·17 (2), 2·41 (2) and 2·60 (2) Å (Jeffrey, Laurie, Moore, Razay & Stone, 1984). These two structures provide further examples of a rare η^1,η^3-bridging *p*-tolylmethylene coordination geometry.

The five carbon atoms comprising the C_5H_5 ring and the six carbon atoms defining the arene ring are essentially coplanar with maximum atomic deviations from coplanarity of 0·02 Å for each ring (see Table 3).* The butterfly structure of the Pt, W, C(1), C(40) bonding network is evident from the dihedral angle of 48·7° between the planes [Pt, W, C(1)] and [Pt, W, C(40)]. The W atom lies 0·14 Å from the [Pt, P(1), P(2)] plane. The BF_4^- anion has nearly tetrahedral geometry having an average B—F distance of 1·34 Å and values for the F—B—F angles in the range of 105 (3)–117 (3)°.

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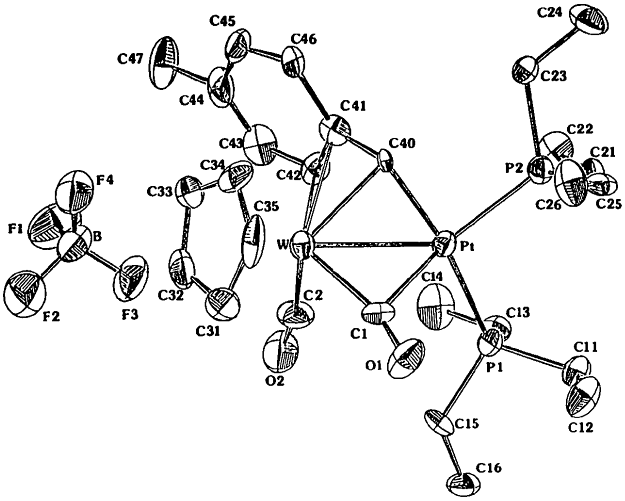

Fig. 1. An *ORTEP* view (ellipsoids at 30% probability) showing the atomic numbering scheme.

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* See deposition footnote.

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Struktur von Di-μ-acetato(*O,O'*)-bis[*N*-(2,3,4-trimethoxybenziliden)-2,4,6-trimethylanilinato-*N,C*]dipalladium(II)

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Abstract. $C_{42}H_{50}N_2O_{10}Pd_2$, $M_r = 955{\cdot}67$, tetragonal, $P4_12_12$, $a = 13{\cdot}164\,(3)$, $c = 24{\cdot}852\,(4)$ Å, $V = 4306{\cdot}9$ Å^3, $Z = 4$, $D_x = 1{\cdot}474$ g cm^{-3}, Cu $K\alpha$, $\lambda = 1{\cdot}54184$ Å, $\mu = 73{\cdot}603$ cm^{-1}, $F(000) = 1952$, $T = 293$ K, final $R = 0{\cdot}032$ for 1704 significant $[I > 3\sigma(I)]$ reflections. In the dinuclear molecule each Pd^{II} atom shows a square-planar coordination and is bonded to the N- and *ortho*-C-atom of the (2,3,4-trimethoxy)benzyl group and to two oxygen atoms of the bridging acetato groups.

Einleitung. Als Teil unserer Untersuchungen über Cyclometallierungsreaktionen von polyheterosubstituierten Aromaten und Schiffschen Basen (Vila, Pereira, Gayoso & Gayoso, 1985; Hiller, Castineiras, Strähle, Suarez, Vila, Gayoso, Gayoso & Garcia Fernandez, 1986) berichten wir im folgenden über die Struktur der Titelverbindung. Mehrkernige Palladium-Komplexe finden besonderes Interesse in der Katalyse (Maugh, 1983).

Experimentelles. Die Reaktion von *N*-(2,3,4-trimethoxybenziliden)-2,4,6-trimethylanilin mit Pd^{II}-acetat und Umkristallisieren in CH_2Cl_2/Hexan ergibt gelbe prismenförmige Kristalle; 0,15 × 0,25 × 0,3 mm; Buerger Präzessionsaufnahmen, Laue-Symmetrie $4/m\ 2/m\ 2/m$, beobachtete Auslöschungsregeln $00l$ nur vorhanden für $l = 4n$, $h00$ nur vorhanden für $h = 2n$, tetragonale Raumgruppe $P4_12_12$ oder $P4_32_12$, erstere bestätigte sich durch die nachfolgenden Rechnungen; Vierkreisdiffraktometer CAD-4 (Fa. Enraf–Nonius, Delft), Cu $K\alpha$, Graphitmonochromator; Verfeinerung der Gitterparameter anhand von 25 genau zentrierten Reflexen ($8 < \theta < 27°$). Registrierung der Reflexintensitäten mit ω/θ scan im Beugungswinkelbereich von $\theta = 3$–$63°$, $h \pm 15$, $k + 15$, $l \pm 28$; alle 60 min drei Kontrollreflexe, keine signifikante Änderung der Intensität; 7483 Reflexe erfasst, LP-Korrektur, empirische Absorptionskorrektur (Azimuth scan), Transmissionsfaktoren 0,766–0,978 (North, Phillips & Mathews, 1968), 2093 symmetrieunabhängige Reflexe ($R_{\rm int} = 0{,}023$), davon 1704 mit $I > 3\sigma(I)$ für die Verfeinerungsrechnungen. Lage des Pd-Atoms aus einer Pattersonsynthese, O-, N-, C- und H-Positionen aus nachfolgenden Differenzfouriersynthesen, Lagen der H-Atome nur in die Strukturfaktorrechnung einbezogen, alle anderen Atomlagen mit anisotropen Temperaturparametern verfeinert, Extinktionskoeffizient in die Verfeinerung einbezogen, $6{,}034 \times 10^{-8}$ (Zachariasen, 1963), $R = 0{,}032$, $wR = 0{,}036$, 254 Parameter, $S = 2{,}329$, $1/w = \sigma_F^2$, $(\Delta/\sigma)_{\max} = 0{,}001$, $\Delta\rho < |0{,}43|$ e Å^{-3}. Die Atomformfaktoren wurden den *International Tables for*

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