Preparation of Heterodinuclear Complexes Containing μ-Alkylidene Ligands

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The regioselective addition of Pt–H or Pt–R (R = Me, CH=CH$_2$) bonds across the M–C triple bonds of alkylidyne ligands affords cationic heterodinuclear complexes containing μ-alkylidene ligands in one step. The syntheses of five alkylidyne and seven η-alkylidene compounds are reported. Addition of a Pt–H$^+$ reagent to a (diethylamino)alkylidyne complex gives a μ-η^1,η^2-(diethylamino)methylidene ligand which is described best as a bridging σ,π-(diethyliminium)methyl ligand. The X-ray structure of this complex is reported: {PtW[μ-η^1,η^2-C(H)(NEt$_2$)](HBpz$_3$)(CO)$_2$(PEt$_3$)$_2$}BF$_4$; monoclinic; $P2_1$; $Z = 2$; $a = 10.991$ (5) Å, $b = 13.956$ (4) Å, $c = 13.684$ (4) Å; $\beta = 95.05$ (3)°.

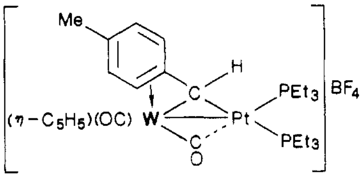
Introduction

Dinuclear complexes containing hydrocarbyl fragments as bridging ligands remain of current interest to chemists because of their potential to exhibit new chemistry and their possible chemical and structural relationship to surface-bound species. Transition-metal complexes containing μ-alkylidene ligands are one such type of compound, and several methods of preparing homo- or heterodinuclear, μ-alkylidene complexes are known.[1]

We have reported recently that the Pt–R bonds of the cationic complexes [*trans*-Pt(PEt$_3$)$_2$(R)(acetone)]BF$_4$, where R is H or Me, add across a C–C triple bond of alkynyl ligands to give cationic homo- and heterodinuclear compounds containing μ-alkenylidene ligands[2] and that a Pt–H bond adds across a W–C triple bond of a *p*-tolylmethylidyne ligand to give a cationic heterodinuclear complex, **1**, containing a μ-η^1,η^3-*p*-tolylmethylidene ligand (see eq 1).[3a] A subsequent X-ray structural determination of **1** confirmed the presence of the η^2-arene coordination to the W atom and revealed a Pt–W single-bond distance of 2.797 (1) Å.[3b] This synthetic method for preparing homo- or heterodinuclear compounds containing different types of bridging hydrocarbyl ligands is based conceptually on the regiospecific addition of a Pt–R bond across an unsaturated bond in a substrate complex. The bridging ligand thus formed places a highly electron-deficient Pt atom in close proximity to the metal atom of the substrate complex so that metal–metal bond formation occurs. Thus, such additions to M–C triple bonds of neutral alkylidyne complexes affords *cationic* μ-alkylidene dinuclear compounds in one step. An alternative two-step procedure effecting this overall conversion and having different synthetic requirements has been effectively employed by Stone et al.[1d-f] In this paper, we report (1) the synthesis of five metal–alkylidyne complexes, (2) the synthesis of five heterodinuclear complexes containing μ-alkylidene ligands via the addition of a Pt–H bond across the M–C triple bonds of alkylidyne complexes, (3) the X-ray crystal structural determination of one such Pt–W compound, and (4) the synthesis of two Pt–W complexes containing μ-alkylidene ligands by the respective addition of Pt–Me or Pt-vinyl bonds across the W–C triple bond of an alkylidyne complex.

$(\eta\text{-}C_5H_5)(OC)_2W{\equiv}CC_6H_4Me\text{-}p$ + [*trans*-PtL$_2$(H)(acetone)]BF$_4$ →

L = PEt$_3$



(1)

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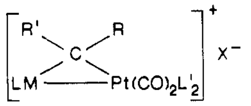
Results and Discussion

When the alkylidyne complexes **2a–f** are treated with the cationic Pt–R species **3a–c**, the cationic heterodinuclear compounds **4a–g** are formed in yields of 43–89% (see eq 2). Each product complex contains a μ-alkylidene ligand formed by regioselective addition of the Pt–R bond across the M–C triple bond of an alkylidyne ligand.

L(OC)$_2$M≡CR′ + [*trans*-Pt(R)L′$_2$(acetone)]$^+$X$^-$ →

	L	M	R′		R	L′	X$^-$
2a	HBpz$_3$	W	Ph	**3a**	H	PEt$_3$	BF$_4^-$, CF$_3$SO$_3^-$
2b	HBpz$_3$	W	furyl	**3b**	Me	PEt$_3$	BF$_4^-$
2c	HBpz$_3$	W	NEt$_2$	**3c**	C(H)=CH$_2$	PMe$_2$Ph	BF$_4^-$
2d	HBpz$_3$	Mo	*p*-tolyl				
2e	HBpz$_3$	W	Me				
2f	C$_5$H$_5$	W	*p*-tolyl				



(2)

	M	R′	R	L	L′	X$^-$
4a	W	Ph	H	HBpz$_3$,	PEt$_3$	BF$_4^-$
4b	W	furyl	H	HBpz$_3$	PEt$_3$	BF$_4^-$
4c	W	NEt$_2$	H	HBpz$_3$	PEt$_3$	BF$_4^-$
4d	Mo	*p*-tolyl	H	HBpz$_3$	PEt$_3$	BF$_4^-$
4e	W	Me	H	HBpz$_3$	PEt$_3$	CF$_3$SO$_3^-$,BF$_4^-$
4f	W	*p*-tolyl	Me	C$_5$H$_5$	PEt$_3$	BF$_4^-$
4g	W	*p*-tolyl	C(H)=CH$_2$	C$_5$H$_5$	PMe$_2$Ph	BF$_4^-$

The alkylidyne complexes **2a–e** are obtained readily as pure solids in 12–84% yield upon treating the corresponding bromoalkylidyne complexes *trans*-Br(OC)$_4$M≡

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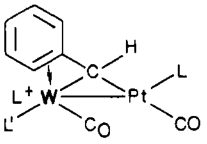
CR′ with potassium hydrotris(1-pyrazolyl)borate, K[HBpz$_3$]. These bromoalkylidyne complexes and the known alkylidyne complex **2f** are prepared according to procedures reported independently by Fischer and Mayr.[4] During the course of this research, complex **2e** was prepared by Stone et al. using a similar procedure.[5] The tungsten complexes **2a**,**b**,**e** exhibit two terminal carbonyl stretching vibrations in the ranges of 1991 ± 4 and 1910 ± 5 cm^{-1}; the molybdenum complex **2d** has analogous absorption bands at 1955 and 1920 cm^{-1}. Complex **2c** contains a (diethylamino)carbyne ligand, and the carbonyl frequencies at 1930 and 1830 cm^{-1} probably indicate considerable resonance delocalization of electron density from the nitrogen atom to the tungsten atom [as is observed in *trans*-$Br(OC)_4W{\equiv}CNEt_2$[6]].

The Pt–R reagents **3a–c** are prepared in situ from the corresponding neutral chloro complexes upon treatment with $AgBF_4$ or $AgCF_3SO_3$ following an analogous procedure reported by Clark et al.[7] The precipitated AgCl is removed by filtration prior to reaction with the alkylidyne complexes.

Dinuclear products **4a–d** have μ-η^1,η^n-alkylidene ligands so that the tungsten atoms attain an 18-electron configuration. In the ^{1}H NMR spectra of these complexes, the appearance of characteristic resonances (showing phosphorus coupling) for the unique bridging alkylidene protons are observed.[3a,8] Complex **4a** contains a μ-η^1,η^3-benzylidene ligand similar to the bridging *p*-tolylmethylidene ligand of compound **1**. In solution, complex **4a** exists as major and minor isomers (in a relative ratio of ca. 3:1) with only the major isomer being present in the solid state. The major isomer has two carbonyl stretching bands at 2020 and 1940 cm^{-1}, an alkylidene proton resonance at δ 7.21, and an ortho-ring proton resonance at δ 7.09. This isomer is assigned the "all-terminal" structure **5** in which a PEt_3–CO ligand isomerization has occurred.



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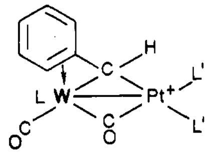

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An analogous ligand isomerization has been observed for a neutral Pt–W μ-alkylidene complex, PtW[μ-C(Me)(OMe)](CO)$_5$ (dppm),[9] and these carbonyl band assignments are consistent with those reported for a related μ-*p*-tolylmethylidyne complex, PtW[μ-C(C$_6$H$_4$Me-*p*)](HBpz$_3$)(CO)$_3$(PMe$_3$).[5a] The minor isomer has a terminal CO band at 1990 cm^{-1} and a bridging CO band at 1840 cm^{-1}. The alkylidene and ortho-ring proton resonances appear at δ 6.85 and 7.15, respectively, thus supporting the bridging structure **6**. These spectroscopic data for the minor isomer are very similar to those observed for complex **1** (which has been characterized structurally).[3]

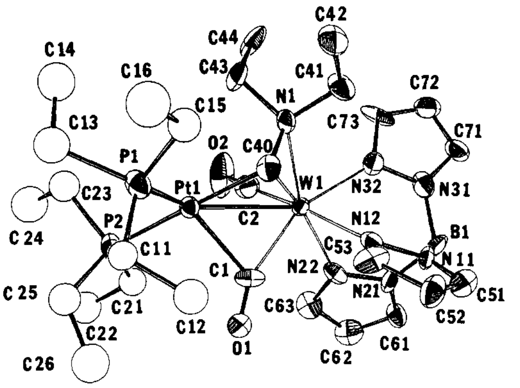
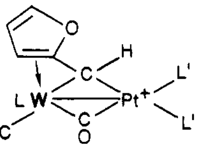


Figure 1. An ORTEP view of the cationic portion of complex **4c** (ellipsoids at 30% probability) showing the atomic numbering scheme.

Complex **4b** contains a furyl substituent on the bridging alkylidene carbon atom. The presence of terminal and bridging carbonyl bands at 1975 and 1835 cm^{-1}, respectively, is consistent with either the μ-η^1,η^3-alkylidene structure **7** or the μ-η^1,η^2-alkylidene structure **8**. We tentatively assign **4b** to structure **7** because the alkylidene proton resonance at δ 6.72 is more similar in chemical shift to the corresponding resonances in analogous η^2-arene complexes (e.g., in complexes **1** and **4a** (minor isomer), this resonance appears at δ 6.74 and 6.85, respectively) than it is to the position of the corresponding resonance of complex **4c** (δ 5.69) where heteroatom donation to the tungsten atom has been established (vide infra). In a related neutral μ-alkylidene complex, PtW[μ-C(C$_6$H$_4$Me-*p*)(cyclopentadienyl)](dppm)(CO)$_4$, a cyclopentadienyl substituent acts as an η^2-arene donor to the tungsten atom similar to the coordination mode shown in **7**.[10]



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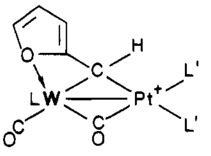

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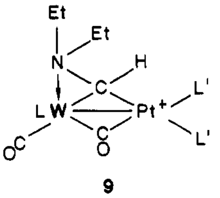
Compound **4c** bears a diethylamino substituent on the bridging alkylidene carbon atom. The ^{1}H NMR spectrum reveals a characteristic alkylidene proton resonance at δ 5.69. However, the observed large anisochronism between the corresponding resonances of the two ethyl groups of the NEt$_2$ substituent (0.81 ppm for the methyl resonances and 1.12 ppm for the methylene resonances) strongly indicate that the nitrogen atom is coordinated to the tungsten atom. These data and the observation of terminal and bridging carbonyl bands at 1900 and 1810 cm^{-1}, respectively, are consistent with the proposed structure **9**, which contains a formal μ-η^1,η^2-C(NEt$_2$)(H)alkylidene ligand, or **10**, which contains a formal σ,π-bridging (diethyl-



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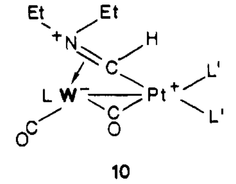

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iminium)methyl ligand. However, if the Pt–H cation **3a** adds to the (diethylamino)carbyne complex **2c** with opposite regiochemistry or by proton transfer from Pt to the NEt_2 group, then different structures for **4c** might be expected.

The molecular structure of **4c** was determined unambiguously by X-ray diffraction. As revealed in Figure 1, the NEt_2 nitrogen atom is coordinated to the tungsten atoms as shown in **9** or **10** to give a formal 18-electron count at W and a 16-electron count at Pt. The Pt atom is bonded to two PEt_3 ligands, a bridging carbonyl ligand, the μ-alkylidene carbon atom, and the tungsten atom. The Pt–P distances of 2.29 (2) and 2.36 (2) Å are not unusual; and, although the Pt(1)–W(1) distance of 2.87 (1) Å is 0.07 Å longer than the Pt–W distance observed in complex **1**, it is ca. 0.03 Å shorter than the Pt–W single-bond distance observed in the neutral μ-alkylidene complex $PtW(\mu\text{-}H)[\mu\text{-}C(H)(C_6H_4Me\text{-}p)(CO)_2(PMe_3)_2(\eta\text{-}C_5H_5)$.[11] The bridging carbonyl ligand has the expected asymmetrical structure with Pt(1)–C(1) and W(1)–C(1) distances of 2.28 (2) and 2.08 (4) Å, respectively, and Pt(1)–C(1)–O(1) and W(1)–C(1)–O(1) angles of 123 (2)° and 155 (2)°, respectively.[3b]

The W atom is coordinated to the $HBpz_3$ ligand, a terminal carbonyl ligand, the Pt atom, and the two bridging ligands. The W–$HBpz_3$ coordination geometry is as expected with the three W(1)–N distances in the range 2.21 (2)–2.28 (3) Å. The W–terminal CO geometry is also typical with a W(1)–C(2) distance of 2.08 (4) Å and a W(1)–C(2)–O(2) angle of 177 (3)°. The overall butterfly shape of the Pt(1), W(1), C(1), C(40) core is evident from the dihedral angle of 52° between the planes defined by [Pt(1), W(1), C(1), O(1)] and [Pt(1), W(1), C(40)]. The corresponding dihedral angle observed in complex **1** is 49°.

The bridging (diethylamino)methylidene ligand has an unusual coordination geometry. The alkylidene carbon atom C(40) is bonded to Pt(1) and W(1) with bond distances of 2.04 (3) and 2.19 (3) Å, respectively, while the nitrogen atom N(1) is bonded to W(1) with a bond distance of 2.22 (2) Å (which falls within the range of W–N distances observed for the $HBpz_3$ coordination). The C(40)–N(1) distance of 1.40 (4) Å indicates a partial multiple bond. The sum of the three angles around C(40) is 273°, indicating some degree of pyramidal geometry. The corresponding value observed for complex **1** is 287°. Pyramidal geometry about N(1) is indicated by a C–N–C angle sum of 341°. The highly asymmetric environment about N(1) accounts for the large anisochronism observed in the ^1H NMR spectrum of **4c** for the two sets of ethyl group resonances. One ethyl substituent is directed toward the highly aromatic groups of the $HBpz_3$ ligand, while the other ethyl substituent is located closer to the PEt_3 ligands.

Even though the alkylidene hydrogen atom bonded to C(40) was not directly observed by X-ray diffraction, the structure of this bridging alkylidene ligand is probably best represented as a resonance hybrid of formal structures **9** and **10**. A significant structural feature is the C(40)–N(1) bond distance of 1.40 (4) Å. This value is very similar to the corresponding C–N distances of 1.392 (6) Å observed in the η^2-dimethyliminium complex $Ni(\eta^2\text{-}H_2C{=}NMe_2)(PPh_3)(Cl)$[12] and of 1.43 (2) Å observed in an η^2-*N*-methylsalicylaldiminium ligand in a mononuclear nickel complex.[13] Within the determined precision limitations, the structure of **4c** presumably represents the first example of a bridging σ,π-(dialkyliminium)methyl ligand. This formulation is related to the σ,π-bridging vinyl structure observed in the complex $PtW[\mu\text{-}C(C_6H_4Me\text{-}p){=}CH_2](CO)_2(PMe_3)_2(\eta\text{-}C_5H_5)$.[11]

Compound **4d** is a close molybdenum analogue to the tungsten complexes **1** and **4a**. The ^1H NMR spectrum of **4d** reveals a bridging alkylidene proton resonance at δ 7.57 and an ortho-ring doublet resonance at δ 6.79, thereby verifying the presence of an $\mu\text{-}\eta^1,\eta^3$-*p*-tolylmethylidene ligand. Carbonyl stretching bands at 1928 and 1844 cm^{-1} indicate terminal and bridging CO ligands, also.

The cationic complex **4e** contains a μ-ethylidene ligand as indicated by the alkylidene proton resonance at δ 4.23 and the alkylidene methyl resonance at δ 1.58 (which exhibits H–H, P–H, and Pt–H coupling). Both terminal and bridging carbonyl ligands are present, also. Although neither the $CF_3SO_3^-$ nor the BF_4^- salts of **4e** are sufficiently stable to permit complete characterization, we believe that neither counterion is coordinated to the tungsten atom, thereby providing only a 16-electron count at this center. This conclusion is supported by the nearly identical ^1H-NMR data observed for both salts and the supposition that BF_4^- is not a coordinating counterion under these conditions. A related μ-ethylidene cluster having a C_5H_5 ligand on tungsten rather than a $HBpz_3$ ligand, $[PtW(\mu\text{-}CHMe)(CO)_2(PMe_3)_2(\eta\text{-}C_5H_5)]BF_4$, converts facilely to an η^2-ethylene complex for the noncoordinating BF_4^- salt but can be stabilized as the μ-ethylidene complex $PtW(O_2CCF_3)(\mu\text{-}CHMe)(CO)_2(PMe_3)_2(\eta\text{-}C_5H_5)$ when a trifluoroacetate counterion is coordinated to tungsten.[14] The stability of **4e** as a μ-ethylidene complex might be attributed to the larger steric bulk and the stronger Lewis basicity of the $HBpz_3$ ligand than that of a C_5H_5 ligand. Both properties of the $HBpz_3$ ligand would inhibit the formation of an agostic W...H–C interaction which is believed to be the first step in the conversion of the related C_5H_5 compounds to η^2-ethylene complexes.[14]

Compound **4f** is obtained by the addition of a Pt–Me bond across the W–C triple bond of the alkylidyne complex **2f**. This synthetic method reduces the conversion of a terminal alkylidyne complex to a heterodinuclear, μ-alkylidene complex from the two step procedure reported by Stone et al. for the analogous complex $\{PtW[\mu\text{-}C(Me)(C_6H_4Me\text{-}p)](CO)_2(PMe_3)_2(\eta\text{-}C_5H_5)\}(CF_3SO_3)$[8b] to one step. For compound **4f**, the bridging alkylidene methyl group proton resonance appears at δ 3.05 and exhibits the expected P–H and Pt–H coupling. Infrared data indicate both terminal and bridging carbonyl ligands. The proton resonance of the ortho-ring proton at δ 5.85 confirms the $\mu\text{-}\eta^1,\eta^3\text{-}C(Me)(C_6H_4Me\text{-}p)$ coordination mode.

Compound **4g** is obtained by the addition of a Pt–vinyl bond across the W–C triple bond of the alkylidyne complex **2f**. Carbonyl stretching bands at 1970 and 1820 cm^{-1} indicate terminal and bridging carbonyl ligands in **4g**, and a vinyl proton resonance centered at δ 3.23 is consistent with a $\mu\text{-}\eta^1,\eta^3$-alkylidene coordination geometry in which the vinyl substituent rather than the *p*-tolyl group is coordinated to tungsten. In a related W–Co complex, $\{CoW[\mu\text{-}C(C_6H_4Me\text{-}p)(CMe{=}CMeH)](CO)_2(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)\}BF_4$, which is prepared by insertion of 2-butyne into the C–H bond of a bridging *p*-tolylmethylidene ligand, the unique vinyl proton resonance appears at δ 3.00.[8a]

The preparation of complexes **4a–g** demonstrates the facile addition of Pt–H or Pt–C bonds across M–C triple bonds of terminal alkylidyne ligands as a direct route to

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heterodinuclear compounds containing bridging alkylidene ligands. We anticipate that other electrophilic reagents might add similarly across M–C multiple bonds to give more unusual complexes containing bridging hydrocarbyl ligands.

Experimental Section

All reactions and other manipulation were performed under dry, prepurified nitrogen at 25 °C unless otherwise stated. Solvents used in reactions were dried according to standard methods and were distilled under nitrogen before use.[15] The reagents oxalyl bromide, potassium hydrotris(1-pyrazolyl)borate, and silver tetrafluoroborate were obtained commercially. The compounds **2f**, *trans*-$Br(OC)_4W{\equiv}CR$, where R = Ph, Me, or NEt_2, and *trans*-$Br(OC)_4Mo{\equiv}C(C_6H_4Me\text{-}p)$ were prepared according to established procedures.[4] The complex *trans*-$Br(OC)_4W{\equiv}C$-(1-furyl) was prepared by using a procedure analogous to that reported for the preparation of similar compounds.[4] The platinum reagents **3a–c** were prepared from the neutral chloro complexes by silver ion abstraction of chloride according to published procedures.[7]

Infrared spectra were recorded on a Perkin-Elmer 727 spectrometer as solutions in a 0.10-mm sodium chloride cavity cell using the solvent as reference and a polystyrene film as a calibration standard. Proton NMR spectra were obtained on JEOL FX-90Q and Bruker AM-400 spectrometers with Me_4Si as an internal reference. optical rotations were measured at the sodium D line by using a Rudolph Research Autopal III polarimeter. Microanalysis was performed by Mic Anal (Tuscon, AZ) or by Galbraith Laboratories, Inc. (Knoxville, TN).

General Preparation of the Complexes $(HBpz_3)(OC)_2M{\equiv}C(R)$ (2a–e). A solution of 0.75–2.00 g of the appropriate complex *trans*-$Br(OC)_4M{\equiv}CR$ in methylene chloride is prepared by dissolving the solid compound in 25 mL of precooled (−20 °C) solvent. To the cooled, rapidly stirred solution was added 1.0 molar equiv of potassium hydrotris(1-pyrazolyl)borate as a solid. Brisk CO evolution occurs immediately, and as the solution was slowly warmed to room temperature, a color change from yellow-orange to orange or red occurred. The solvent was removed at 25 °C under reduced pressure, and the residue was extracted with 4 × 50 mL of ether. Filtration of the extracts was followed by removal of the solvent in vacuo to yield the crude alkylidyne complex as an orange to brown solid. The crude solid was chromatographed on an alumina column (Brockman Activity 1, 80–200 mesh, 18 mm × 100 mm). A yellow or orange band was eluted with hexane–ether (1:1, v/v) in all cases. Crystallization from hexane–ether (2:1, v/v) in each case (except for **2b**) produced analytically pure product. Complex **2b** was isolated as a yellow powder after chromatography. The detailed characterization data for each complex are provided below.

$(HBpz_3)(OC)_2W{\equiv}C(C_6H_5)$ (2a): orange crystals; yield 84%; mp 131–133 °C dec; IR (CH_2Cl_2) ν(CO) 1987 (vs), 1905 (vs) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.22 (d of d, 3, $C_3H_3N_2$), 7.31 (m, 5, C_6H_5), 7.65 (m, 3, $C_3H_3N_2$), 8.01 (m, 3, $C_3H_3N_2$). Anal. Calcd for $C_{18}H_{15}BN_6O_2W$: C, 39.89; H, 2.79. Found: C, 39.54; H, 2.91.

$(HBpz_3)(OC)_2W{\equiv}C$(2-furyl) (2b): yellow powder; yield 27%; mp 159–161 °C; IR (hexane) ν(CO) 1990 (vs), 1915 (vs) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.50 (s, br, 1, B–H), 6.15 (m, 3, $C_3H_3N_2$), 6.30 (m, 1 furyl H), 6.45 (m, 1, furyl H), 7.26 (m, 1, furyl H), 7.65 (m, 3, $C_3H_3N_2$), 8.03 (m, 3, $C_3H_3N_2$). Anal. Calcd for $C_{16}H_{13}BN_6O_3W$: C, 36.15; H, 2.46; N, 15.98. Found: C, 36.08; H, 2.40; N, 15.81.

$(HBpz_3)(OC)_2W{\equiv}CNEt_2$ (2c): green-yellow crystals; yield 12%; mp 189–193 °C dec; IR (CH_2Cl_2) ν(CO) 1930 (vs), 1830 (vs) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.38 (t, 6, CH_3, J_{HH} = 7.14 Hz), 3.41 (q, 4, CH_2, J_{HH} = 7.14.Hz), 4.45 (s, br, 1, B–H), 6.16 (m, 3, $C_3H_3N_2$), 7.61 (m, 3, $C_3H_3N_2$), 7.78 (m, 3, $C_3H_3N_2$). Anal. Calcd for $C_{16}H_{20}BN_7O_2W$: C, 35.78; H, 3.75. Found: C, 35.51; H, 3.80.

$(HBpz_3)(OC)_2Mo{\equiv}C(C_6H_4Me\text{-}p)$ (2d): orange crystals; yield 45%; mp 160.5–161.5 °C; IR (pentane) ν(CO) 1955 (vs), 1920 (vs) cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 2.34 (s, 3, CH_3), 6.19 (m, 3, $C_3H_3N_2$), 7.08 (d, 2, aryl H, J_{HH} = 8.35 Hz); 7.41 (d, 2, aryl H, J_{HH} = 8.35 Hz), 7.64 (m, 3, $C_3H_3N_2$), 7.89 (m, 3, $C_oH_3N_2$). Anal. Calcd for $C_{19}H_{17}BN_6O_2Mo$: C, 48.75; H, 3.66; N, 17.95. Found: C, 49.04; H, 3.77; N, 17.71.

$(HBpz_3)(OC)_2W{\equiv}CCH_3$ (2e): green-yellow crystals; yield 52%; mp 117–118 °C; IR (pentane) ν(CO) 1995 (m), 1910 (vs) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.41 (s, 3, CH_3), 6.17 (m, 3, $C_oH_3N_2$), 7.63 (m, 3, $C_3H_3N_2$), 7.95 (m, 3, $C_3H_3N_2$). Anal. Calcd for $C_{13}H_{13}BN_6O_2W$: C, 32.53; H, 2.73. Found: C, 32.30; H, 2.97.

General Preparation of the Heterodinuclear Compounds 4a–g. To a stirred solution of 0.1–0.25 g of the appropriate alkylidyne complex **2a–f** in 10 mL of acetone was added 1.0 molar equiv of **3a**, **3b**, or **3c** in 3–5 mL of acetone. Over a period of 30 s to 5 min the solution color changed from yellow-orange to brown-orange. Stirring was continued for a period of 12 h, after which time the solvent was removed in vacuo. Trituration of the gummy residue with 4 × 10 mL of ether produced a yellow to red solid, which was washed with 2 × 10 mL of pentane and dried under reduced pressure. Complex **4a** was crystallized from methylene chloride–pentane (3:1, v/v). Complex **4b** was isolated as yellow-brown microcrystals by precipitation from methylene chloride solution with hexane. Complex **4c** was crystallized from chloroform–ether (2:1, v/v). Complex **4d** was crystallized from tetrahydrofuran–hexane (4:1, v/v). Complex **4e** was prepared and was characterized in acetone-d_6 solution. Complex **4f** was crystallized from tetrahydrofuran–hexane. Complex **4g** was isolated as yellow microcrystals by precipitation from methylene chloride with addition of diethyl ether. Detailed characterization data for complexes **4a–g** are as follows.

$\{PtW[\mu\text{-}\eta^1,\eta^3\text{-}C(H)(C_6H_5)(HBpz_3)(CO)_2(PEt_3)_2\}BF_4$ (4a): orange crystals; yield 43%; mp 128–131 °C dec. Major isomer: IR (CH_2Cl_2) ν(CO) 2020 (s), 1940 (vs) cm^{-1}; H NMR ($CDCl_3$) δ 0.705 (d of t, 9, CH_3, J_{HH} = 7.8 Hz, J_{PH} = 17.4 Hz), 1.05 (d of t, 9, CH_3, J_{HH} = 7.8 Hz, J_{PH} = 17.4 Hz), 1.465 (m, 12, CH_2, J_{HH} = 7.8 Hz), 4.6 (s, br, 1, B–H), 6.39 (m, 3, $C_3H_3N_2$), 7.09 (d, 1, C_6H_5, J_{HH} = 6.8 Hz), 7.21 (m, 1 μ-CH, J_{PH} = 7.5 Hz), 7.44 (m, 3, $C_3H_3N_2$), 7.66 (m, 4, C_6H_5), 7.84 (s, br, 1, $C_3H_3N_2$), 7.93 (m, 1, $C_oH_3N_2$), 8.07 (s, br, 1, $C_oH_3N_2$). Minor isomer: IR (CH_2Cl_2) ν(CO) 1990 (m), 1840 (w, br) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.121 (d of t, 9, CH_3, J_{HH} = 8.4 Hz, J_{PH} = 16.6 Hz), 1.230 (d of t, 9, CH_3, J_{HH} = 7.8 Hz, J_{PH} = 16.6 Hz), 1.98 (m, 6, CH_2, J_{HH} = 8.4 Hz, J_{PH} = 14.8 Hz), 2.20 (m, 6, CH_2, J_{HH} = 7.8 Hz, J_{PH} = 16.6 Hz), 4.6 (s, br, 1, B–H), 6.22 (m, 3, $C_3H_3N_2$), 6.85 (d of d, 1, μ-CH, J_{PH} = 8 Hz, J_{PH} = 8.1 Hz), 7.15 (d, 1, C_6H_5, J_{HH} = 6.8 Hz), 7.48 (m, 3, $C_3H_3N_2$), 7.66 (m, 4, C_6H_5), 7.93 (m, 1, $C_3H_3N_2$), 8.01 (m, 1, $C_3H_3N_2$), 8.12 (m, 1, $C_3H_3N_2$). Anal. Calcd for $C_{30}H_{46}B_2F_4N_6O_2P_2WPt$: C, 33.95; H, 4.38; N, 7.92. Found: C, 34.18, H, 4.54; N, 7.73.

$\{PtW[\mu\text{-}\eta^1,\eta^3\text{-}C(H)(2\text{-}furyl)](HBpz_3)(CO)_2(PEt_3)_2\}BF_4$ (4b): green-yellow solid; yield 49%; mp 113–117 °C dec; IR (CH_2Cl_2) ν(CO) 1975 (m), 1835 (s, br) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.03–1.28 (m, 18, CH_3), 1.94–2.33 (m, 12, CH_2), 4.40 (s, 1, B–H), 5.93 (s, 1, C_4H_3O), 6.28 (s, 1, $C_3H_3N_2$), 6.30 (s, 1, $C_3H_3N_2$), 6.33 (s, 1, $C_3H_3N_2$), 6.72 (d, 1, μ-CH, J_{PH} = 8.5 Hz), 7.04 (s, 1, C_4H_3O), 7.60 (s, 1, $C_3H_3N_2$), 7.63 (s, 1, C_4H_3O), 7.65 (m, 2, $C_3H_3N_2$), 7.84 (s, 1, $C_3H_3N_2$), 7.93 (s, 1, $C_3H_3N_2$), 8.04 (s, 1, $C_3H_3N_2$). Anal. Calcd for $C_{28}H_{44}B_2F_4N_6O_3P_2PtW$: C, 31.99; H, 4.22; N, 7.99. Found: C, 32.48; H, 4.41; N, 7.82.

$\{PtW[\mu\text{-}\eta^1,\eta^2\text{-}C(H)(NEt_2)(HBpz_3)(CO)_2(PEt_3)_2\}BF_4$ (4c): crimson crystals; yield 44%; mp 154.5–155 °C; IR (CH_2Cl_2) ν(CO) 1900 (m), 1810 (vs) cm^{-1}, ^{1}H NMR ($CDCl_3$) δ 0.55 (t, 3, CH_3, J_{HH} = 7.14 Hz), 1.145 (d of t, 9, CH_3, J_{HH} = 7.57 Hz, J_{PH} = 15.2 Hz), 1.25 (d of t, 9, CH_3, J_{HH} = 7.7 Hz, J_{PH} = 14.5 Hz), 1.361 (t, 3, CH_3, J_{HH} = 7.16 Hz), 2.08 (d of q, 6, CH_2, J_{HH} = 7.6 Hz, J_{PH} = 37 Hz), 2.34 (d of q, 6, CH_2, J_{HH} = 7.7 Hz, J_{PH} = 38 Hz), 2.58 (q, 2, CH_2, J_{HH} = 7.2 Hz), 3.70 (m, 2, CH_2), 4.68 (s, br, 1, B–H), 5.69 (d of d, 1, μ-CH, J_{HH} = 5.8 Hz, J_{PH} = 10.3 Hz), 6.32 (t of t, 3, $C_3H_3N_2$), 7.70 (t of d, 3, $C_3H_3N_2$), 7.96 (t of d, 3, $C_3H_3N_2$). Anal. Calcd for $C_{34}H_{51}B_2F_4N_7O_2P_2WPt$: C, 31.84; H, 4.87; N, 9.28. Found: C, 31.92; H, 4.97; N, 9.32.

$\{PtMo[\mu\text{-}\eta^1,\eta^3\text{-}C(H)(C_6H_4Me\text{-}p)](HBpz_3)(CO)_2(PEt_3)_2\}BF_4$ (4d): red microcrystals; yield 89%; mp 143–148 °C; IR (CH_2Cl_2) ν(CO) 1928 (s), 1844 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.05–1.28 (m, 18, CH_3, J_{HH} = 7.5, 7.6 Hz), 1.91–2.28 (m, 12, CH_2, J_{HH} = 7.5, 7.6 Hz), 4.38 (s, 1, B–H), 6.08 (s, 1, $C_3H_3N_2$), 6.21 (s, 1, $C_3H_3N_2$), 6.31 (s, 1, $C_3H_3N_2$), 6.73 (s, 1, $C_3H_3N_2$), 6.79 (d, 1, C_6H_4, J_{HH} = 8.4 Hz), 6.90 (d, 1, C_6H_4, J_{HH} = 6.9 Hz), 6.95 (d, 1, C_6H_4, J_{HH} = 7.1 Hz), 7.08 (d, 1, C_6H_4, J_{HH} = 8.4 Hz), 7.55 (d, 1, $C_3H_3N_2$, J_{HH} = 2.2 Hz),

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[15] Lenhert, P. G.; Lukehart, C. M.; Sacksteder, L. A. *J. Am. Chem. Soc.* **1986**, *108*, 793–800.

Table I. Crystallographic Data for Complex 4c

formula	$C_{28}H_{51}B_2F_4N_7O_2P_2PtW$
mol wt	1056.32 daltons
cryst system	monoclinic
space group	$P2_1$
a, Å	10.991 (5)
b, Å	13.956 (4)
c, Å	13.684 (4)
β, deg	95.05 (3)
V, Å^3	2090.8
Z	2
D_{calcd}, g cm^{-3}	1.678
cryst size, mm	0.30 × 0.25 × 0.10
μ(Mo Kα), cm^{-1}	63.5
X radiatn	λ = 0.71073 Å (graphite monochromator)
temp, °C	23 (1)
hkl space explored	$h,k,\pm l$
2θ range, deg	0–50
no. of reflns measd	4056
no. of unique data	3815
no. of unique data used	3692
scan type	ω–θ technique
scan mode	variable scan rate from 2 to 20°/min (in ω)
bkgd time	peak counting time/bkgd counting time rate = 2:1
abs cor	empirical psi-scan correctn
transmissn factors	
max	0.999
min	0.466
av	0.822
no. of stds used	3
intensity decay	none
no. of variables refined	320
R	0.055
R_w[a]	0.062

[a] $R_w = [[\sum w(|F_o| - |F_c|)^2]/\sum w|F_o|^2]^{1/2}$ where w is $1/\sigma(F_o)^2$.

7.65 (d, 1, $C_3H_3N_2$, J_{HH} = 1.9 Hz), 7.68 (d, 1, $C_3H_3N_2$, J_{HH} = 1.8 Hz), 7.57 (d, 1, μ-CH, J_{PH} = 5.1 Hz), 7.81 (s, 1, $C_3H_3N_2$), 7.90 (s, 1, $C_3H_3N_2$). Anal. Calcd for $C_{31}H_{48}B_2F_4N_6O_2P_2MoPt$: C, 37.71; H, 4.90; N, 8.51. Found: C, 37.45; H, 4.96; N, 8.41.

{PtW[μ-η^1,η^3-C(H)(CH$_3$)](HBpz$_3$)(CO)$_2$(PEt$_3$)$_2$}(CF$_3$SO$_3$ or BF$_4$) (4e). $CF_3SO_3^-$ salt: IR (CH_2Cl_2) ν(CO) 1932 (m), 1810 (m) cm^{-1}. ^{1}H NMR (acetone-d_6) δ 1.17–1.26 (m, 18, CH_3, J_{HH} = 7.5 Hz, J_{PH} = 16.9 Hz), 1.58 (d of d of d, μ-C-CH_3, J_{HH} = 2.8 Hz, J_{PH} = 7.8 Hz, J_{PtH} = 15.5 Hz), 1.90 (m, 6, CH_2), 2.26 (m, 6, CH_2, J_{HH} = 7.8 Hz), 4.23 ("q", 1, μ-CH, J_{HH} = 2.8 Hz), 6.46–6.60 (m, 3, $C_3H_3N_2$), 7.86–8.14 (m, 3, $C_3H_3N_2$), 8.58–8.70 (m, 3, $C_3H_3N_2$). BF_4^- salt: IR (CH_2Cl_2) ν(CO) 1932 (m), 1810 (m) cm^{-1}; ^{1}H NMR (acetone-d_6) 1.15–1.32 (m, 18, CH_3, J_{HH} = 7.5 Hz), 1.59 (m, 3, μ-C–CH_3, J_{HH} = 2.8 Hz, J_{PH} = 7.6 Hz, J_{PtH} = 15 Hz), 1.68–2.38 (m, 12, CH_2), 4.24 (m, 1 μ-CH, J_{HH} = 2.7 Hz, J_{PH} = 8 Hz), 6.48–8.80 (m, 9, $C_3H_3N_2$).

{PtW[μ-η^1,η^3-C(CH$_3$)(C$_6$H$_4$Me-*p*)](η-C$_5$H$_5$)(CO)$_2$(PEt$_3$)$_2$}BF$_4$ (4f): yellow microcrystals; yield 85%; mp 105.5–112.5 °C dec; IR (CH_2Cl_2) ν(CO) 1952 (s), 1810 (m, br) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.94 (d of t, 9, CH_3, J_{HH} = 7.5 Hz, J_{PH} = 17.2 Hz), 1.12 (d of t, 9, CH_3, J_{HH} = 7.5 Hz, J_{PH} = 15.9 Hz), 1.70–2.10 (m, 12, CH_2), 2.37 (s, 3, CH_3), 3.05 (d of d, 3, μ-CCH_3, J_{PH} = 2.1 Hz, 6.1 Hz, J_{PtH} = 11.6 Hz), 4.64 (s, 5, C_5H_5), 5.85 (d, 1, C_6H_4, J_{HH} = 5.9 Hz), 7.09 (d, 1, C_6H_4, J_{HH} = 6.3 Hz), 7.31 (d, 1, C_6H_4, J_{HH} = 8.9 Hz), 7.37 (d, 1, C_6H_4, J_{HH} = 9 Hz). Anal. Calcd for $C_{28}H_{45}BF_4O_2P_2PtW$: C, 35.72; H, 4.82. Found: C, 36.03; H, 5.10.

{PtW[μ-η^1,η^3-C(CH=CH$_2$)(C$_6$H$_4$Me-*p*)](η-C$_5$H$_5$)(CO)$_2$(PMe$_2$Ph)$_2$}BF$_4$ (4g): yellow microcrystals; yield 75%; mp 145–148 °C dec; IR (CH_2Cl_2) ν(CO) 1970 (vs), 1820 (, br) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.10 (d, 3, CH_3, J_{PH} = 20 Hz), 1.28 (d, 3, CH_3, J_{PH} = 20 Hz), 1.43 (d, 3, CH_3, J_{PH} = 20 Hz), 1.65 (d, 3, CH_3, J_{PH} = 20 Hz), 2.38 (s, 3, CH_3), 3.23 (d of d of d, 1, μ-C(C*H*=CH$_2$), J_{PH} = 42 Hz, J_{HH} = 11 Hz, 3 Hz), 5.30 (s, 5, C_5H_5), 6.78 (m, 2, μ-C(CH=C*H*$_2$), J_{PH} = 18 Hz, J_{HH} = 3, 6 Hz), 7.10–7.60 (m, 14, C_6H_5, C_6H_4). Anal. Calcd for $C_{33}H_{37}BF_4O_2P_2PtW$: C, 39.90; H, 3.75. Found: C, 40.27; H, 3.58.

Structural Determination of Complex 4c. Complex **4c** was prepared as stated above and was crystallized as red plates. Collection of the X-ray data, including Lorentz, polarization, and empirical absorption corrections were performed by Molecular Structure Corporation, College Station, TX, as a commerical, technical service. An Enraf-Nonius CAD 4 computer-controlled, kappa-axis diffractometer was used. Relevant crystallographic data are provided in Table I. Solution (via a sharpened Patterson function) and refinement of the structure were performed with the X-RAY 67 programs as implemented and updated on the Vanderbilt DEC-10 computer. Specific references to the control software and the solution and refinement methods and software have been reported previously.[16]

Table II. Atomic Positional Parameters after Rounding for Complex 4c[a]

atom	M	x	y	z
Pt(1)	0.92	0.36054 (82)	0.57832 (8)	0.16654 (6)
W(1)	0.92	0.23455 (7)	0.75000	0.21433 (6)
P(1)		0.50801 (66)	0.47235 (52)	0.22692 (53)
P(2)		0.32180 (65)	0.541431 (47)	0.00731 (51)
F(1)		0.8237	0.6556	0.5257
F(2)		0.6005	0.6895	0.5075
F(3)		0.7143	0.8104	0.5348
F(4)		0.7203	0.7267	0.3936
O(1)		0.4025 (14)	0.7533 (14)	0.0417 (12)
O(2)		0.0220 (17)	0.6409 (16)	0.0926 (20)
N(1)		0.2397 (18)	0.6444 (12)	0.3362 (14)
N(11)		0.3417 (15)	0.9512 (11)	0.3015 (12)
N(12)		0.3697 (18)	0.8543 (14)	0.2869 (15)
N(21)		0.1808 (17)	0.9676 (12)	0.1554 (14)
N(22)		0.1959 (15)	0.8774 (13)	0.1210 (12)
N(31)		0.1135 (24)	0.9243 (15)	0.3194 (16)
N(32)		0.0989 (19)	0.8336 (13)	0.2976 (14)
C(1)		0.3509 (20)	0.7300 (17)	0.1042 (17)
C(2)		0.0961 (26)	0.6776 (18)	0.1318 (22)
C(11)		0.6529 (22)	0.4962 (18)	0.1803 (19)
C(12)		0.6899 (26)	0.6098 (22)	0.1967 (22)
C(13)		0.4860 (30)	0.3326 (24)	0.1988 (26)
C(14)		0.3716 (33)	0.2962 (26)	0.2415 (27)
C(15)		0.5363 (25)	0.4767 (20)	0.3660 (21)
C(16)		0.6513 (32)	0.4058 (30)	0.4153 (29)
C(21)		0.2329 (22)	0.5893 (22)	−0.0789 (19)
C(22)		0.2085 (29)	0.5493 (23)	−0.1863 (24)
C(23)		0.2367	0.4017	0.0201
C(24)		0.1699	0.3748	−0.0798
C(25)		0.4673	0.4818	−0.0436
C(26)		0.5138	0.5684	−0.0994
C(40)		0.3531 (25)	0.6475 (17)	0.2976 (19)
C(41)		0.2439 (26)	0.6862 (18)	0.4396 (17)
C(42)		0.3064 (29)	0.6233 (19)	0.5201 (18)
C(43)		0.1724 (37)	0.5468 (17)	0.3289 (25)
C(44)		0.0288 (26)	0.5551 (16)	0.3412 (28)
C(51)		0.4392 (22)	1.0006 (18)	0.3389 (19)
C(52)		0.5415 (27)	0.9407 (18)	0.3444 (19)
C(53)		0.4931 (23)	0.8426 (19)	0.3143 (17)
C(61)		0.1431 (22)	1.0268 (16)	0.0859 (18)
C(62)		0.1281 (24)	0.9805 (21)	−0.0012 (22)
C(63)		0.1600 (21)	0.8834 (18)	0.0215 (19)
C(71)		0.0294 (26)	0.9552 (19)	0.3754 (20)
C(72)		−0.0464 (26)	0.8825 (20)	0.3849 (21)
C(73)		−0.0020 (21)	0.8099 (22)	0.3385 (18)
B(1)		0.2126 (27)	0.9852 (19)	0.2727 (27)
B2		0.7273	0.6884	0.5060
Pt(2)	0.08	0.9709 (12)	0.779 (11)	0.8208 (19)
W(2)	0.08	1.0917 (13)	0.7771 (11)	0.6461 (12)

[a] Estimated standard deviations in parentheses.

The y coordinate of the tungsten atom was undefined and was fixed at $^1/_4$. All nonhydrogen atoms were located from a difference synthesis. The electron densities of the four carbon atoms C23, C24, C25, and C26 (which comprise two ethyl groups attached to P2) were located in extended ellipsoidal regions of space (ca. 2 Å in x, ca. 3 Å in y and ca. 1 Å in z) due to an apparent disorder. Refinement of these positions led to positional drifts which did not converge. The positions of these four carbon atoms were fixed at maximum electron density locations which afforded P2–C

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[16] Lenhert, P. G.; Lukehart, C. M.; Warfield, L. T. *Inorg. Chem.* **1980**, *19*, 2343–2347.

Table III. Value of Selected Interatomic Distances (Å) and Angles (deg) for Complex 4c[a]

Interatomic Distances			
Pt(1)-W(1)	2.871 (10)	P(1)-C(15)	1.90 (3)
Pt(1)-P(1)	2.29 (2)	P(2)-C(21)	1.80 (3)
Pt(1)-P(2)	2.359 (14)	P(2)-C(23)	1.845 (7)
Pt(1)-C(1)	2.28 (2)	P(2)-C(25)	1.86 (2)
Pt(1)-C(40)	2.04 (3)	O(1)-C(1)	1.12 (3)
W(1)-N(1)	2.22 (2)	O(2)-C(2)	1.06 (4)
W(1)-N(12)	2.25 (3)	N(1)-C(40)	1.40 (4)
W(1)-N(22)	2.21 (2)	N(1)-C(41)	1.53 (3)
W(1)-N(32)	2.28 (3)	N(1)-C(43)	1.55 (3)
W(1)-C(1)	2.08 (4)	N(31)-B(1)	1.56 (4)
W(1)-C(2)	2.08 (4)	C(41)-C(42)	1.52 (4)
W(1)-C(40)	2.19 (3)	C(43)-C(44)	1.61 (5)
P(1-)-C(11)	1.80 (3)	Pt(2)-W(2)	2.83 (4)
P(1)-C(13)	2.00 (4)		

Interatomic Angles			
W(1)-Pt(1)-P(1)	142.7 (2)	Pt(1)-P(2)-C(23)	106.7 (3)
W(1)-Pt(1)-P(2)	118.4 (2)	Pt(1)-P(2)-C(25)	110.4 (3)
W(1)-Pt(1)-C(1)	45.8 (6)	C(40)-N(1)-C(41)	113 (2)
W(1)-Pt(1)-C(40)	49.4 (7)	C(40)-N(1)-C(43)	116 (2)
P(1)-Pt(1)-P(2)	98.8 (3)	C(41)-N(1)-C(43)	112 (2)
Pt(1)-W(1)-C(1)	51.9 (7)	Pt(1)-C(1)-O(1)	123 (2)
Pt(1)-W(1)-C(2)	79.4 (8)	W(1)-C(1)-O-(1)	155 (2)
Pt(1)-W(1)-C(40)	45.2 (7)	W(1)-C(2)-O(2)	177 (3)
Pt(1)-P(1)-C(11)	111.9 (9)	Pt(1)-C(40)-N(1)	115 (2)
Pt(1)-P(1)-C(13)	119.4 (10)	N(1)-C(41)-C(42)	115 (2)
Pt(1)-P(1)-C(15)	112.8 (9)	N(1)-C(43)-C(44)	113 (2)
Pt(1)-P(2)-C(21)	115.4 (9)		

[a] Estimated standard deviations in parentheses.

distances of ca. 1.85 Å and C–C distances of 1.54 Å. For the atoms C23, C24, C25, and C26, the respective electron densities at each location were 2.9, 1.8, 2.0 and 2.3 electrons/Å^3. Isotropic temperature factors of 7.0 or 10.0, respectively, were assigned to these carbon atoms depending on whether the atom was a methylene or a methyl carbon. The parameters of these atoms were used in the calculations but were not refined.

Two areas of electron density were located from the difference map which did not come within a 4.1-Å contact distance of any of the other atoms of the cationic Pt–W cluster complex. Because the bond distance between the two areas of electron density was found to be approximately 2.8 Å in the early stages of the refinement, the peaks were arbitrarily named W(2) and Pt(2). On the basis of the magnitude of the peak electron densities, both atoms were assigned population parameters of $M = 0.2$. Refinement of the M values of Pt(2) and W(2) yielded population parameters of ca. 0.08 for both atoms. While the possibility that these peaks might represent a pair of hydrogen-bonded water molecules cannot be excluded, the microanalytical and high-field proton NMR data acquired from precisely this single crystalline sample strongly favors the disordered lattice model.

Refinement proceeded to convergence with isotropic refinement of atoms C(11)–C(22) and fixed parameters (after initial refinement) for the atoms of the BF_4^- counterion. Refinement of the opposite enantiomer using the full data set led to an increase in the values of the final R and R_w factors of 0.004, indicating that the proper enantiomer was refined. The specific rotation, $[\alpha]_D^{25}$, of a solution prepared from a single crystal of **4c** was measured to be +57.1° (c 0.14, $CHCl_3$). The specific rotation of a solution prepared from a bulk sample of single crystals gave zero rotation, thus indicating that **4c** was crystallized as equal numbers of enantiomeric crystals. The maximum and minimum densities on the final difference map were 2.39 e Å^{-3} [near W(2)] and −1.11 e Å^{-3} [near Pt(1)]. A list of atomic positional parameters after rounding is provided in Table II. Selected interatomic distances and angles are given in Table III. A complete lising of final atomic positional and thermal parameters, interatomic distances and angles, selected least-squares planes data, and final observed and calculated structure factors are included as supplementary material.

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Supplementary Material Available: Tables of final atomic positional and thermal parameters, interatomic distances and angles, and selected least-squares planes data (5 pages); a listing of final observed and calculated structure factors (13 pages). Ordering information is given on any current masthead page.