6000 *Organometallics* **2007,** *26,* 6000−6008

Polymeric Alkylidene-Bridged Platinum Complex $[\{Pt_2(\mu\text{-}Cl)_2\{\mu\text{-}C(OBu)Me\}_2\}_n]$: Synthesis, Reactivity, and Quantum Chemical Calculations

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Received August 13, 2007

$H_2[PtCl_6]\cdot 6H_2O$ in dried *n*-BuOH was found to react with an excess of bis(trimethylsilyl)acetylene (BTMSA), yielding the polymeric alkylidene-bridged platinum complex $[\{Pt_2(\mu\text{-}Cl)_2\{\mu\text{-}C(OBu)Me\}_2\}_n]$ (**3**). Reactions of complex **3** with monodentate N, P, and S donors afforded dinuclear alkylidene-bridged complexes *trans*-$[\{PtCl(L)\}_2\{\mu\text{-}C(OBu)Me\}_2]$ (2-Mepy, **5a**; 4-Mepy, **5b**; 2-Brpy, **5c**; PPh_3, **6a**; PPh_2(4-py), **6b**; tht, **7**) (tht = tetrahydrothiophene) in yields between 51 and 92%. Owing to a *syn* and *anti* arrangement of the butoxy substituents, complexes **5**−**7** were obtained as diastereomeric mixtures. All comlexes were characterized by means of microanalysis and IR and NMR spectroscopy. Furthermore, X-ray diffraction analyses were performed for the complexes **5a**−**c** and **6a**,**b**, exhibiting central Pt_2C_2 rings with Pt−Pt distances between 2.573(1) and 2.681(1) Å. Quantum chemical studies of **6a** using the AIM theory gave evidence of the bonding in the Pt_2C_2 moiety in terms of four-centered bonds.

1. Introduction

Carbenes are neutral species containing a divalent carbon atom with only six valence electrons having a singlet or a triplet ground-state spin multiplicity. In general, these compounds are highly reactive and commonly known as transient intermediates in organic reactions.[1] Stabilization of singlet carbenes may be achieved by π-donor substituents (N, S, ...)[2] as especially in Arduengo carbenes and stabilization of triplet carbenes by steric protection[3] of the carbene C atom. Furthermore, one of the major challenges of organometallic chemistry is the stabilization of highly reactive carbon intermediates, such as carbenes, by metal complex formation and to make use of these complexes in stoichiometric and, especially, in catalytic transformations. Since the first synthesis of a stable transition metal carbene (alkylidene) complex by Fischer and Maasböl in 1964,[4] this exciting field continuously gains in importance. Metal carbene complexes play a key role in many organic reactions and catalytic processes, especially in the olefin metathesis reaction (e.g., Noble Prize laureates 2005: Y. Chauvin, R. R. Schrock, R. H. Grubbs).[5] The multitude of transition metal alkylidene complexes may be devided into four types (Chart 1): (a) *Fischer-type complexes* of (typically) late transition metal atoms in low oxidation states ($M = W^0$, Mo^0, Fe^0, ...) having π-donor substituents on the carbene C atoms (ER_n = OR, NR_2, ...) and π-acceptor co-ligands (L = CO, Cp, ...);[6] (b) *Schrock-type complexes* of typically early transition metals in higher oxidation states ($M = Ta^V$, Nb^V, W^{VI}, ...) having non-π-donor groups on the carbene C atoms and co-ligands L = Cp, PR_3, ...;[7] (c) *N-heterocyclic carbene (NHC) complexes* of main and transition metals in various oxidation states; NHC ligands are pronounced σ-donor ligands with only little, generally negligible, π-acceptor character;[8] (d) *complexes with bridging alkylidene ligands* (both heteroatom functionalized and nonfunctionalized) having usually metal−metal bonds in addition.[9] As a result of the bridging coordination mode, the alkylidene ligands lose some of their unsaturation and, therefore, the very high reactivity compared to their mononuclear analogues.[10] One of the most valuable methods

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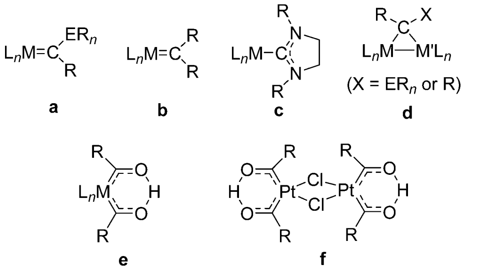
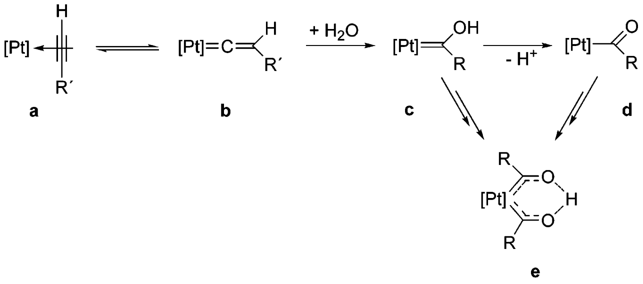
10.1021/om7007138 CCC: $37.00

Chart 1. Types of Alkylidene Complexes (a−d) and Metalla-*β*-diketones (e, f); See Text



Scheme 1. Proposed Mechanism for the Formation of Platina-*β*-diketones[a]



[a] The ligand spheres and the overall charges of complexes are not specified; R = CH_2R' (taken from ref 14b).

for the preparation of alkylidene-bridged complexes comprises the use of diazomethane or analogous compounds.[11] Also Fischer-type alkylidene complexes were found to react with alkene platinum(0) complexes, yielding bimetallic alkylidene-bridged complexes (Stone, 1980).[12] Up to now, no homometallic dinuclear alkylidene-bridged platinum complexes were known.

In general, hydroxycarbene complexes proved to be of higher reactivity and lower stability than analogous alkoxycarbene complexes. But they may be severely stabilized by an intramolecular O−H···O hydrogen bond to an acyl ligand in *cis* position, resulting in the formation of metalla-β-diketones. Those of the Lukehart type (Chart 1, e) are electronically saturated (18 ve, ve = valence electrons), kinetically inert complexes of transition metals in low oxidation states (M = Mn, Re, Fe, ...) with CO and Cp co-ligands.[13] In contrast, platina-β-diketones (Chart 1, f) are electronically unsaturated (16 ve), kinetically labile complexes exhibiting a reactivity completely different from Lukehart's metalla-β-diketones.[14]

Platina-β-diketones $[Pt_2\{(COR)_2H\}_2(\mu\text{-}Cl)_2]$ (Chart 1, f) were prepared by the reaction of hexachloroplatinic acid in *n*-butanol with silylated alkynes $R'C{\equiv}CSiMe_3$, whereas after reduction of Pt^{IV} to Pt^{II} and cleavage of the Si−C≡ bond, likely, a platinum(II) complex with a terminal alkyne ligand is formed (Scheme 1, a) that undergoes a tautomerization, yielding a vinylidene complex (b). Then, reaction with water and subsequent deprotonation could result in the formation of hydroxycarbene and acyl species (c/d), being the two building blocks of the platina-β-diketones (e).[14b] Using bis(trimethylsilyl)acetylene (BTMSA), it was found that slight changes in the reaction conditions led, instead of the formation of the platina-β-diketone $[Pt_2\{(COMe)_2H\}_2(\mu\text{-}Cl)_2]$ (**1**),[14] to the formation of the Fischer-type alkylidene complex *cis*-$[PtCl_2\{C(OBu)Me\}_2]$ (**2**)[15] or to a polymeric, homometallic alkylidene-bridged platinum complex, $[\{Pt_2(\mu\text{-}Cl)_2\{\mu\text{-}C(OBu)Me\}_2\}_n]$ (**3**). Here we report the synthesis and the characterization of this novel coordination polymer. Furthermore, its reactivity toward monodentate N, P, and S ligands will be discussed, yielding dinuclear alkylidene-bridged platinum complexes *trans*-$[\{PtCl(L)\}_2\{\mu\text{-}C(OBu)Me\}_2]$ (**5**−**7**). Quantum chemical calculations were performed to gain a deeper understanding of the bonding modes in such platinum complexes.

2. Results and Discussion

2.1. Reactions of $H_2[PtCl_6]\cdot 6H_2O$ with Bis(trimethylsilyl)acetylene in *n*-BuOH. 2.1.1. Synthesis of $[\{Pt_2(\mu\text{-}Cl)_2\{\mu\text{-}C(OBu)Me\}_2\}_n]$ (3). The "classical" procedure to synthesize the platina-β-diketone **1** is a two-step procedure comprising the reduction of hexachloroplatinic acid in *n*-butanol at about 80 °C, yielding Zeise's acid with an *n*-butene ligand, $H[PtCl_3(\eta^2\text{-}H_2C{=}CHEt)]$, followed by the addition of bis(trimethylsilyl)acetylene at room temperature (Scheme 2, path a). The addition of a small amount of water may result in an increase of the yield of **1** depending on the quality of the hexachloroplatinic acid. When the alkyne is added at 100 °C in the presence of a certain amount of water (see Experimental Section), the platina-β-diketone **1** is formed in very high yields (>90%) (path b). In contrast, the same reaction in well-dried *n*-butanol resulted in the formation of the alkylidene-bridged coordination polymer **3** (path c). Complex **3** was isolated as yellow, air-sensitive microcrystals in 75% yield. In the solid state it is thermally highly stable (T_{dec} = 135 °C). Furthermore, it should be mentioned that the one-pot reaction of $H_2[PtCl_6]\cdot 6H_2O$ with bis(trimethylsilyl)acetylene in dried *n*-BuOH at 40 °C yielded the Fischer-type alkylidene complex **2** (path d), which was found to react in wet solvents yielding quantitatively **1**.[15]

2.1.2. Spectroscopic Characterization. The identity of the polymeric alkylidene-bridged platinum complex **3** has been confirmed by microanalysis and IR (ν_{CO} = 1151 cm^{-1}) and NMR spectroscopic measurements. Not surprisingly, the coordination polymer **3** is hardly soluble in typical organic solvents such as chloroform, methylene chloride, and acetone, but it proved to be freely soluble in dmso. Most likely, the high donor capability of dmso (cf. DN(dmso) = 29.8; DN = donor

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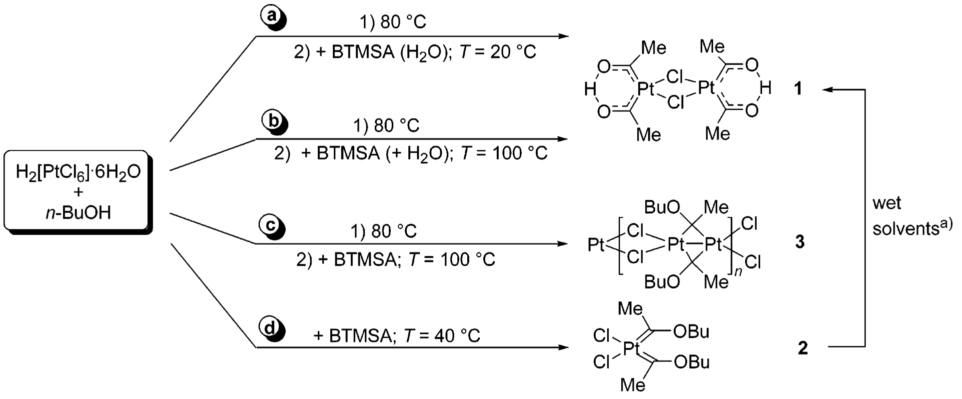
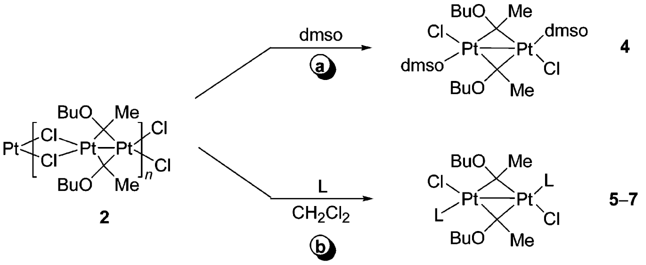
Scheme 2. Reactivity of $H_2PtCl_6 \cdot 6H_2O$ in *n*-BuOH with BTMSA



[a] $CHCl_3$, Et_2O, CH_3NO_2, ...

Scheme 3. Synthesis of the Dinuclear Alkylidene-Bridged Platinum Complexes *trans*-[{PtCl(dmso)}$_2${*μ*-C(OBu)Me}$_2$] (4) and *trans*-[{PtCl(L)}$_2${*μ*-C(OBu)Me}$_2$] (5−7)



	5a	5b	5c	6a	6b	7
L	2-Mepy	4-Mepy	2-Brpy	PPh_3	PPh_2(4-py)	thf

number)[16] gives rise to a cleavage of the chloro bridges, forming the dinuclear complex *trans*-[{PtCl(dmso)}$_2${*μ*-C(OBu)Me}$_2$] (**4**) (Scheme 3, path a). In deuterated dmso the ^1H and ^{13}C NMR spectra showed the expected signals and gave proof for the chemical equivalence of the two alkylidene ligands. The protons of the CC*H*$_3$ group resonate at 2.24 ppm, being high-field shifted by about 0.50 ppm compared to the CC*H*$_3$ protons in the Fischer-type complex *cis*-[PtCl$_2${C(OBu)Me}$_2$] (**2**), having terminal alkylidene ligands (δ 2.74 ppm).[15] The resonance of the carbene C atom was found as a broad signal at 191.2 ppm, that is, compared to the resonance in **2** (δ 272.9 ppm), significantly high-field shifted.[15] This meets the expectation: Due to the greater unsaturation of terminal alkylidene ligands, the carbene C resonances are found in a range from 200 to 400 ppm (in exceptional cases up to 500 ppm), whereas those of bridging alkylidene ligands appear in a typical range between 100 and 210 pm.[10]

2.2. Reactivity of the Coordination Polymer 3 toward Monodentate N, P, and S Ligands. 2.2.1. Synthesis of *trans*-[{PtCl(L)}$_2${*μ*-C(OBu)Me}$_2$] (5−7). According to the above-mentioned reaction of **3** with dmso (Scheme 3, path a), we investigated whether monodentate N, P, and S ligands are capable of analogous bridge cleavage reactions. Thus, the coordination polymer **3** was found to react with a stoichiometric amount of pyridines (2-Mepy, 4-Mepy, 2-Brpy), phosphines (PPh_3, PPh_2(4-py)), and tetrahydrothiophene (tht) at −70 °C, forming dinuclear complexes *trans*-[{PtCl(L)}$_2${*μ*-C(OBu)Me}$_2$] (**5**−**7**) within several minutes (path b). All these complexes were isolated as yellow, moderately air-sensitive substances in good to excellent yields (51−92%). In the solid state they decompose between 117 and 147 °C. Their identities have been unambiguously confirmed by microanalysis, NMR spectroscopic measurements. and single-crystal X-ray diffraction analyses (**5a**−**c**, **6a**,**b**).

2.2.2. Structural Characterization. Suitable crystals for X-ray diffraction analyses of the dinuclear alkylidene-bridged platinum complexes *trans*-[{PtCl(L)}$_2${*μ*-C(OBu)Me}$_2$] (L = 2-Mepy, **5a**; 4-Mepy, **5b**; 2-Brpy, **5c**) have been obtained from methylene chloride/diethyl ether solutions. The complexes crystallize in discrete molecules without unusual intermolecular contacts. All these dinuclear complexes exhibited crystallographically imposed inversion symmetry. Because of the structural similarities, the structure of complex **5c** is shown as an example in Figure 1. Selected bond lengths and angles for all three complexes are given in Table 1.

The platinum centers exhibit in good approximation a square-planar coordination (sum of angles: 360.0°, **5a**; 359.1°, **5b**; 360.1°, **5c**; largest deviation from the $Pt_2C_2Cl_2N_2$ complex plane: Pt, 0.009(5) Å, **5a**; Pt, 0.016(1) Å, **5b**; Pt, 0.019(1) Å, **5c**). The butoxy substituents are arranged in an *anti* position relative to the complex plane. All structures revealed a tilting of the pyridine rings relative to the complex plane (interplanar angle: $\gamma = 62.4(2)-78.8(2)°$). This may be the result of steric and electronic interactions (π-type back-donation).[17] The Pt−N (2.127(4)−2.146(4) Å) and Pt−Cl (2.363(1)−2.368(1) Å) bond distances are longer than those in other platinum(II) complexes having pyridine ligands (median: 2.031 Å, lower/upper quartile: 2.010/2.081 Å, $n = 2125$, n = number of observations) and chloro ligands (median: 2.314 Å, lower/upper quartile: 2.298/2.355 Å, $n = 3734$),[18] showing a large *trans* influence of the alkylidene ligands. The Pt−C1 bond lengths in complexes **5** *trans* to the pyridine ligands are slightly shorter (2.016(4)−2.028(5) Å) than those *trans* to the chloro ligands (2.052(3)−2.068(4) Å), reflecting only slight differences in the *trans* influence (Cl > py).[19] But, as expected, all Pt−C bonds (2.016(4)−2.068(4) Å) are significantly longer than those in Fischer-type platinum complexes having terminal alkylidene ligands (median: 1.991 Å, lower/upper quartile: 1.920/2.012 Å, $n = 13$).[18] The Pt−Pt distances in **5a**−**c** (2.573(1)−2.579(1) Å) are comparable with those found in [{Pt(CO)}$_3${*μ*-C(OMe)(4-MeC$_6$H$_4$)}$_3$] and [Pt$_2$W(CO)$_6${P(C$_6$H$_{11}$)$_3$}$_2${*μ*-C(OMe)(4-

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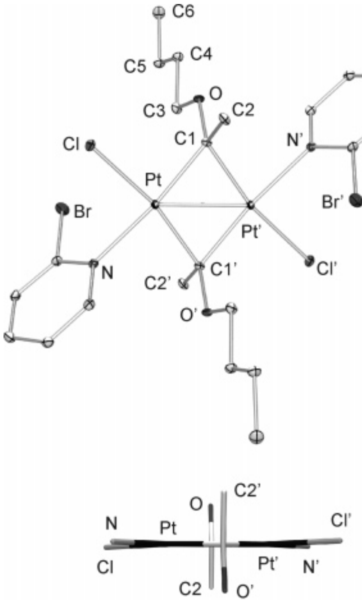

Figure 1. Molecular structure of *trans*-[{PtCl(2-Brpy)}$_2${μ-C(OBu)Me}$_2$] (**5c**) with ellipsoids at the 30% probability level and stick model viewed along the $Pt_2C_2Cl_2N_2$ plane. H atoms are omitted for clarity.

Table 1. Selected Distances (Å) and Angles (deg) of the Dinuclear Alkylidene-Bridged Platinum Complexes *trans*-[{PtCl(L)}$_2${μ-C(OBu)Me}$_2$] (L = 2-Mepy, 5a; 4-Mepy, 5b; 2-Brpy, 5c)

	5a	5b	5c
Pt−Pt′	2.573(1)	2.579(1)	2.578(1)
Pt−N	2.127(4)	2.129(3)	2.146(4)
Pt−Cl	2.363(1)	2.368(1)	2.364(2)
Pt−C1	2.028(5)	2.018(3)	2.016(4)
Pt−C1′	2.066(5)	2.052(3)	2.068(4)
C1−C2	1.510(7)	1.511(4)	1.509(6)
C1−O	1.365(6)	1.375(4)	1.373(5)
C1−Pt−N	85.7(2)	85.6(1)	84.7(2)
N−Pt−Cl	84.0(1)	85.1(1)	84.5(1)
Cl−Pt−C1	88.2(2)	87.9(1)	89.1(1)
O−C1−C2	106.8(4)	106.7(3)	106.8(3)
Pt−C1−Pt′	77.9(2)	78.7(1)	78.3(2)
γ^a	76.9(2)	62.4(2)	78.8(2)

[a] Angle between the plane of the pyridine ring atoms and the $Pt_2C_2Cl_2N_2$ plane (complex plane).

MeC$_6$H$_4$)}] (Pt−Pt 2.619(1)−2.632 Å).[9a,12d] The carbene C atoms adopt a distorted tetrahedral configuration; as expected,[10] the Pt−C1−Pt′ angles are relatively small (77.9(2)−78.7(1)°), whereas the O−C1−C2 angles are 106.7(3)−106.8(3)°.

The dinuclear alkylidene-bridged complexes *trans*-[{PtCl(L)}$_2${μ-C(OBu)Me}$_2$] (L = PPh$_3$, **6a**; PPh$_2$(4-py), **6b**) crystallized from chloroform/diethyl ether as **6a**·2CHCl$_3$ and **6b**·2CHCl$_3$ in well-shaped yellow crystals that were suitable for single-crystal X-ray diffraction analysis (space group: $P\bar{1}$). The crystals consist of discrete centrosymmetric molecules without unusual intermolecular contacts. The molecular structures of the two complexes are very similar, and that of **6b** is shown in Figure 2. Selected bond lengths and angles of the two complexes are given in Table 2.

In general, the structural features of the dinuclear alkylidene-bridged complexes with phosphine ligands (**6a**,**b**) are close to those with pyridine ligands (**5a**−**c**). In accordance with the high *trans* influence of phosphines,[19] the Pt−Cl bond lengths *trans* to these ligands are significantly longer than those *trans* to the chloro ligands (2.165(8)/2.139(6) versus 1.988(8)/2.001(7) Å **6a**,**b**). Also this gives rise to longer Pt−Pt bonds (2.681(1)/2.658(1) Å **6a**,**b**) compared to those in complexes **5a**−**c** (2.573(1)−2.579(1) Å). As for complexes **5a**−**c** the carbene C atoms in complexes **6a**,**b** exhibit also a distorted tetrahedral arrangement (Pt−C1−Pt′ 80.3(3)°/79.8(2)°, O−C1−C2 108.3(7)°/105.9(6)°).

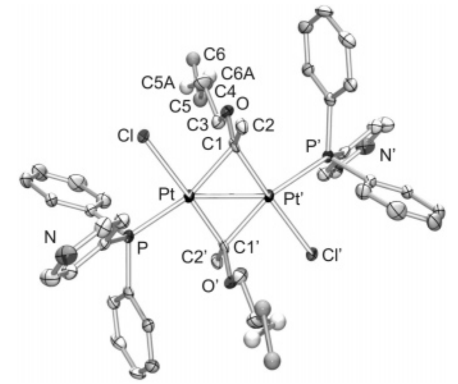

Figure 2. Molecular structure of *trans*-[{PtCl{PPh$_2$(4-py)}}$_2${μ-C(OBu)Me}$_2$] (**6b**) in crystals of **6b**·2CHCl$_3$ with ellipsoids at the 30% probability level. H atoms are omitted and the disorderd positions of C5/C5A and C6/C6A are shown as balls.

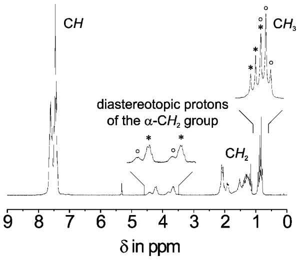

Figure 3. ^{1}H NMR spectrum (200 MHz, CD$_2$Cl$_2$) of *trans*-[{PtCl(PPh$_3$)}$_2${μ-C(OBu)Me}$_2$] (**6a**). The signals marked with ° and *, respectively, show the diastereomeric complexes of **6a** where the butoxy substituents are arranged in an *anti* or *syn* configuration.

Table 2. Selected Distances (Å) and Angles (deg) of the Dinuclear Alkylidene-Bridged Platinum Complexes *trans*-[{PtCl(L)}$_2${μ-C(OBu)Me}$_2$] (L = PPh$_3$, 6a; PPh$_2$(4-py), 6b)

	6a·2CHCl$_3$	**6b**·2CHCl$_3$
Pt−Pt′	2.681(1)	2.658(1)
Pt−P	2.349(2)	2.325(2)
Pt−Cl	2.414(2)	2.403(2)
Pt−C1	1.988(8)	2.001(7)
Pt−C1′	2.165(8)	2.139(6)
C1−C2	1.52(2)	1.55(1)
C1−Pt−P	93.9(2)	95.1(2)
P−Pt−Cl	83.8(1)	82.7(1)
Cl−Pt−C1	82.7(2)	82.1(2)
O−C1−C2	108.3(7)	105.9(6)
Pt−C1−Pt′	80.3(3)	79.8(2)

2.2.3. Spectroscopic Characterization. ^{1}H, ^{13}C, and ^{195}Pt NMR spectroscopic data for complexes **5**−**7** and additionally ^{31}P NMR data for complexes **6** gave further proof for the constitution of the complexes as determined by X-ray crystallography. NMR investigations (^{1}H, ^{13}C, ^{31}P, ^{195}Pt) revealed the existence of two diastereomers in solution (CD$_2$Cl$_2$). As an example, the spectroscopic characterization of [{PtCl(PPh$_3$)}$_2${μ-C(OBu)Me}$_2$] (**6a**) will be discussed in more detail. The ^{1}H NMR spectrum of **6a** is shown in Figure 3. The assignment of the signals was further confirmed by ^{1}H,^{1}H and ^{13}C,^{1}H COSY experiments. It can be clearly seen that two isomers, most likely the diastereomers *trans*-[{PtCl(PPh$_3$)}$_2${μ-C(OBu)Me}$_2$] with *syn*- (point group C_2) and *anti*-arranged (point group C_i) butoxy

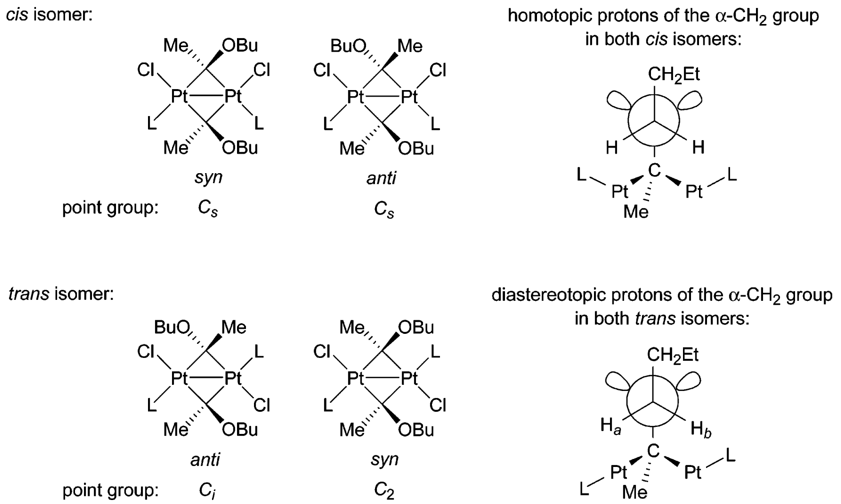

Figure 4. Possible isomers of the complexes *trans*-[{PtCl(L)}$_2${μ-C(OBu)Me}$_2$] (**5**−**7**). There are four isomers due to the mutual *cis* and *trans* positions of the terminal ligands (Cl, L) and the *syn* and *anti* positions of the substituents on the bridging carbene carbon atoms.

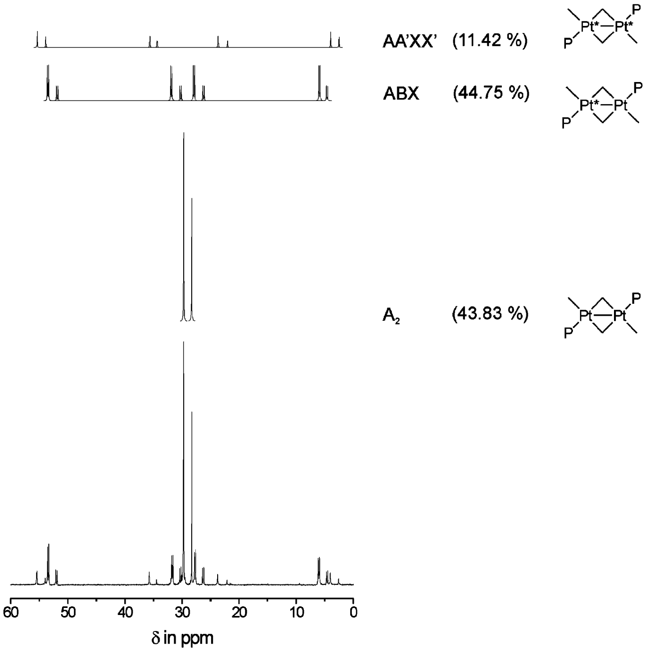

Figure 5. Observed and simulated ^{31}P NMR spectra of the diastereomeric mixture of *trans*-[{PtCl(PPh$_3$)}$_2${μ-C(OBu)Me}$_2$] (**6a**) along with the spin systems (A, B = ^{31}P; X = ^{195}Pt).

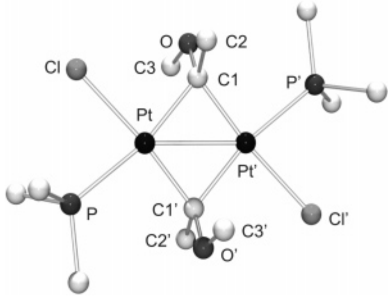

Figure 6. Calculated structure of *trans*-[{PtCl(PMe$_3$)}$_2${μ-C(OMe)-Me}$_2$] (**6a′**). Selected distances (Å) and angles (deg): Pt−Pt′ 2.714, Pt−P 2.392, Pt−Cl 2.485, Pt−C1 2.166, Pt−C1′ 2.047, Pt−C1−Pt′ 80.1, C1−Pt−Cl 84.2, C1′−Pt−P 94.0.

Table 3. Selected NMR Data (δ in ppm, J in Hz) for the Dinuclear Alkylidene-Bridged Platinum Complexes *trans*-[{PtCl(L)}$_2${μ-C(OBu)Me}$_2$] (5)

	L	isomer[a]	$\delta(P)$	^1J(Pt,Pt)	^1J(Pt,P)	^2J(Pt,P)	^3J(P,P)
5a	PPh$_3$	*syn*	28.2	5680	3854	328	21
		anti	29.6	5900	3848	326	18
5b	PPh$_2$(4-py)	*syn*	26.6	5830	3797	336	23
		anti	28.1	6050	3805	331	18

[a] Assignment is based on crystallization experiments.

substituents in the ratio 1:3, were formed. In accordance with this the protons of the α-CH$_2$ groups were found to be diastereotopic (Figure 4). Contrary to this, in the requisite *cis* isomers (point group: C_s) the α-CH$_2$ protons would have been homotopic (Figure 4).

The ^{31}P NMR spectrum of **6a** exhibits for both isomers two multiplets symmetrically to their centers of 28.2 and 29.6 ppm. Due to the natural abundance of the NMR-active platinum isotope ^{195}Pt (nat. abundance: 33.8%, $I = 1/2$), each multiplet has to be analyzed as a superposition of the three spin systems A$_2$, ABX, and AA′XX′ (A, B = ^{31}P; X = ^{195}Pt). The measured ^{31}P NMR spectrum and the simulation of each spin system (using the PERCH program package)[20] for each isomer of **6a** are shown in Figure 5. Thus, a full set of platinum−phosphorus coupling constants for both isomers of the complexes *trans*-[{PtCl(L)}$_2${μ-C(OBu)Me}$_2$] (L = PPh$_3$, **6a**; PPh$_2$(4-py), **6b**) could be obtained (Table 3). Because all experiments to separate the two diastereomers by fractional crystallization failed, the assignment of the isomers remains tentative. X-ray structure investigations of several selected crystals obtained in this way indicated that the major diastereomer is that which has been structurally characterized (*anti* isomer). The ^1J(Pt,Pt) coupling constants of both isomers (*syn*/*anti*) in complexes **6** were between 5680 and 6050 Hz. The coupling constants in the *syn* isomers are slightly smaller (by 220 Hz) than in the *anti* isomers. But, in general, they are significantly larger than those found in other alkylidene platinum complexes reported in the literature (^1J(Pt,Pt) = 1748−3115 Hz),[9a,12d] indicating strong Pt−Pt interactions.

2.3. Theoretical Calculations. The complex *trans*-[{PtCl-(PMe$_3$)}$_2${μ-C(OMe)Me}$_2$] (**6a′**) (point group: C_i) has been calculated at the DFT level of theory to give insight into the nature of bonding in complexes of type **5**−**7**. The calculated structure of **6a′** is shown in Figure 6. Selected bond lengths and angles are given in the figure caption. For the calculation of **6a′** the structural data of **6a** were used as a starting point

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(20) *PERCH-NMR-Software*, Version 1/2000; University of Kuopio, 1993−2000.

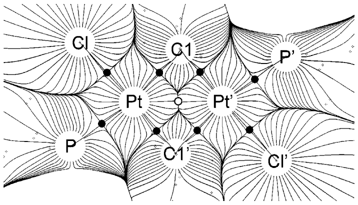


Figure 7. Gradient paths of electron density $\rho(r)$ (QTAIM) in the calculated structure of *trans*-[{PtCl(PMe$_3$)}$_2${μ-C(OMe)Me}$_2$] (**6a′**) (● bond critical point {3, −1}, ○ ring critical point {3, 1}).

Table 4. Selected Parameters (in au) of the Bond Critical Points of 6a′ between Pt and Its Directly Bonded Atoms (C, Cl, P) and of the Ring Critical Point in the Center of the Molecule[a]

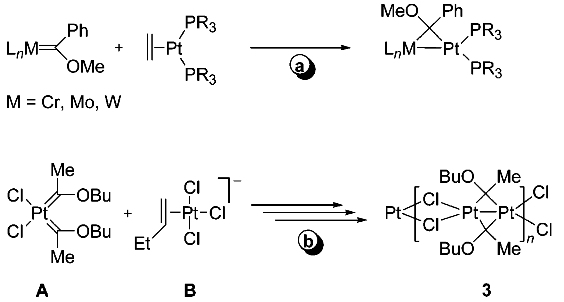
bcp/rcp	ρ	$\nabla^2\rho$	ϵ	G/ρ	H/ρ
Pt−C1	0.14	0.14	0.06	0.7	−0.25
Pt−C1′	0.11	0.12	0.05	0.64	−0.27
Pt−Cl	0.07	0.17	0.03	0.85	−0.66
Pt−P	0.09	0.11	0.08	0.64	−0.30
Pt$_2$C$_2$	0.05	0.14		0.8	−0.63

[a] $\rho(r)$, electron density; $\nabla^2\rho$, Laplacian of the electron density; ϵ, ellipticity; G, kinetic energy density; H, total energy density.

and for comparison of the final structural parameters to judge the quality of calculations. Although **6a** and **6a′** differ in the phosphine ligand (PPh$_3$ versus PMe$_3$) and in the carbene substituent (OBu versus OMe), the calculated and experimental structures were found to be in good agreement (deviation from Pt−Pt: 0.033 Å; Pt−P: 0.043 Å; Pt−C1: 0.071 Å). The topological analysis of the electronic charge density $\rho(r)$ using the quantum theory of atoms in molecules (QTAIM) exhibited bond critical points (bcp's) and a ring critical point (rcp) as shown in Figure 7. The values found at the bond critical points show typical behavior for bonds incorporating heavy atoms (Table 4).[21] The electron density is small, the Laplacian is positive and small, $G/\rho < 1$, and $H/\rho < 0$. There was no bond path and no bond critical point between the two platinum centers, indicating that a 2c−2e Pt−Pt bond does not exist. This is in analogy to the well-investigated dicobaltoctacarbonyl [{Co(CO)$_3$}$_2$(μ-CO)$_2$] (**8**), where the QTAIM analysis also showed no Co−Co bond path.[22] Both in **6a′** and in **8** the metal fragments (PtCl(PMe$_3$) versus Co(CO)$_3$) are open-shell systems ($M = 2$) and the doubly bridged (μ-carbene versus μ-CO) dinuclear complexes are closed-shell systems. Inspection of the occupied canonical orbitals gives an understanding of the bonding in the Pt$_2$C$_2$ moiety in terms of four-centered bonds, whereas the three highest molecular orbitals are of antibonding Pt−Pt character, quite analogous to **8**.

2.4. Conclusion. In the scope of the work presented here, the synthesis of the coordination polymer [{Pt$_2$(μ-Cl)$_2${μ-C(OBu)Me}$_2$}$_n$] (**3**) and its reactivity toward N, P, and S ligands L were explored resulting in Pt−Cl−Pt bridge cleavage in the formation of dinuclear alkylidene-bridged complexes *trans*-[{PtCl(L)}$_2${μ-C(OBu)Me}$_2$] (**5**−**7**) as diasterereomeric mixtures with *syn*- and *anti*-arranged butoxy substituents. These results led to the assumption that the Pt$_2${μ-C(OBu)Me}$_2$ units in the coordination polymer **3** also have *syn*- and *anti*-arranged butoxy substituents. When the bridging carbene ligands are regarded as dianions, then the platinum atoms in the complexes **3**−**7** exhibit the oxidation state +III.

Scheme 4. Proposed Mechanism for the Formation of Polymeric Alkylidene-Bridged Platinum Complex 3



In the late 1970s Stone et al. showed that mixed metal alkylidene-bridged complexes can be prepared by reactions of Fischer-type alkylidene complexes with olefin platinum(0) compounds (Scheme 4, path a).[12] There is likely an analogous way of formation of the alkylidene-bridged coordination polymer **3** (Scheme 4, path b), having in mind that Zeise's acid analogous complex H[PtCl$_3$(η^2-C$_4$H$_8$)][14] and the Fischer-type alkylidene complex *cis*-[PtCl$_2${C(OBu)Me}$_2$] (**1**)[15] were proven to be intermediates in this reaction.

To conclude, bis(alkylidene) platinum complexes can be easily prepared in reactions of hexachloroplatinic acid with bis(trimethylsilyl)acetylene (BTMSA). The reactions can be directed such that mononuclear platinum complexes (**2**), having two terminal alkylidene ligands (Scheme 2, d),[15] or a polymeric platinum complex (**3**), having bridging alkylidene ligands (Scheme 2, c), can be obtained. This complex **3** proved to be a suitable starting complex to prepare, with a wide variety of coligands L, the first homometallic dinuclear platinum complexes *trans*-[{PtCl(L)}$_2${μ-C(OBu)Me}$_2$] (**5**−**7**), which have two bridging alkylidene ligands.

3. Experimental Section

3.1. General Comments. All reactions and manipulations were carried out under argon using standard Schlenk techniques. Solvents were dried prior to use: CHCl$_3$, CH$_2$Cl$_2$ over CaH$_2$, diethyl ether, *n*-pentane over Na/benzophenone, and acetone over 4 Å molecular sieves. The NMR spectra (^{1}H, ^{13}C, ^{31}P, ^{195}Pt) were recorded at 27 °C on Varian Gemini 200, VXR 400, and Unity 500 spectrometers. Chemical shifts are relative to solvent signals (CDCl$_3$, δ_H 7.24, δ_C 77.0; CD$_2$Cl$_2$, δ_H 5.32, δ_C 53.8; dmso, δ_H 2.49, δ_C 39.5) as internal references; δ(^{31}P) and δ(^{195}Pt) are relative to external H$_3$PO$_4$ (85%) (δ_P 0.0) and H$_2$[PtCl$_6$] in D$_2$O (δ_{Pt} 0.0), respectively. The coupling constants in higher order spin systems were calculated using the PERCH 2000 program package.[20] When necessary, assignments of signals were verified by ^{1}H,^{1}H and ^{13}C,^{1}H COSY experiments. Microanalyses (C, H, S, Cl) were performed in the Microanalytical Laboratory of the University of Halle using for C, H, and S a CHNS-932 (LECO) as well as a VARIO EL (Elementaranalysensysteme) elemental analyzer and for Cl a volumetric analysis (Schöninger). IR spectra were recorded on a Mattson 5000 Galaxy FT-IR spectrometer using KBr pellets. Hexachloroplatinic acid (Degussa) and phosphines (Aldrich, Fluka, Merck) were commercially available.

3.2. Synthesis of [Pt$_2${(COMe)$_2$H}$_2$(μ-Cl}$_2$] (1), Optimized Procedure. On the basis of the procedure given in ref 14a a solution of H$_2$[PtCl$_6$]·6H$_2$O (6.0 g, 11.6 mmol) in *n*-BuOH (12 mL) was heated with stirring at 80 °C for 3 h, whereupon the color changed from orange to brown. Then, at this temperature water (4 mL) and bis(trimethylsilyl)acetylene (BTMSA; 10.0 g, 58.7 mmol) were added and the resulting mixture was heated again (up to 100−

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[21] Macchi, P.; Sironi, A. *Coord. Chem. Rev.* **2003**, *238*−239, 383−412.

[22] (a) Heijser, W.; Baerends, E. J.; Ros, P. *Faraday Symp. Chem. Soc.* **1980**, *14*, 211−234. (b) Leung, P. C.; Coppens, P. *Acta Crystallogr.* **1983**, *B39*, 535−542. (c) Low, A. A.; Kunze, K. L.; MacDougall, P. J.; Hall, M. B. *Inorg. Chem.* **1991**, *30*, 1079−1086. (d) Kluge, O.; Finger, M.; Reinhold, J. *Inorg. Chem.* **2005**, *44*, 6494−6496.

117 °C) until an exothermic reaction occurred. Within several minutes the color of the solution changed from brown to yellow, indicating the completeness of the reaction. Then, the solution was cooled to 0 °C, whereupon yellow crystals of **1** precipitated. These were filtered off, washed with diethyl ether (10 mL), and dried in vacuo. A further batch is obtained by reducing the volume of the mother liquor. Yield: 3.43 g (93%). For spectroscopic data see ref 14a.

3.3. Synthesis of [{Pt$_2$(*μ*-Cl)$_2${*μ*-C(OBu)Me}$_2$}$_n$] (3). A solution of $H_2[PtCl_6]\cdot 6H_2O$ (6.0 g, 11.6 mmol) in dried *n*-BuOH (18 mL) was heated to 80 °C and kept for 3 h at this temperature, whereupon the color changed from orange to light brown. BTMSA (10.0 g, 58.7 mmol) was added, and the resulting mixture was heated again until an exothermic reaction occurred. Within 1 min the color of the solution changed from light to dark brown. Then the solution was cooled to room temperature and the volume was reduced in vacuo until a yellow-colored solid precipitated. After 2 days at 5 °C the yellow, air-sensitive powder was filtered off, washed with methylene chloride (10 mL), and dried in vacuo. Yield: 2.86 g (75%). T_{dec}: 135 °C. Anal. Found: C, 21.44; H, 3.54; Cl, 10.72. $C_{12}H_{24}Cl_2O_2Pt_2$ (661.38) requires: C, 21.79; H, 3.66; Cl, 10.72.

NMR Spectroscopic Data for trans-[{PtCl(dmso)}$_2${*μ*-C(OBu)Me}$_2$] (4). ^{1}H NMR (500 MHz, dmso-*d*$_6$): *δ* 0.84 (t, ^3J(H,H) = 7.48 Hz, 6H, C*H*$_3$, Bu), 1.33 (m, 4H, *γ*-C*H*$_2$), 1.60 (m, 4H, *β*-C*H*$_2$), 2.24 (s(br), 6H, C*H*$_3$), 3.98 (m, 4H, α-C*H*$_2$). ^{13}C NMR (125 MHz, dmso-*d*$_6$): *δ* 13.6 (s, *C*H$_3$, Bu), 18.7 (s, *γ*-*C*H$_2$), 30.6 (s, *β*-*C*H$_2$), 40.1 (m, *C*H$_3$), 75.1 (m, α-*C*H$_2$), 191.2 (s, $C_{carbene}$). ^{195}Pt NMR (107 MHz, dmso-*d*$_6$): *δ* −4804 (s). IR: *ν* 2956(m), 2934(m), 2871(m), 2083(w), 1151(s), 1016(s), 613(s) cm^{-1}.

3.4. Reactivity of Complex 3 toward Pyridines. To a suspension of **3** (100 mg, 0.15 mmol) in methylene chloride (3 mL) was added a solution of the corresponding pyridine derivative L (L = 2-Mepy, 4-Mepy, 2-Brpy; 0.30 mmol) in methylene chloride (1 mL) with stirring at −70 °C. Within 10 min a pale yellow solution was formed. To this reaction mixture was added diethyl ether (10 mL). The resulting yellow precipitate of *trans*-[{PtCl(L)}$_2${*μ*-C(OBu)Me}$_2$] (L = 2-Mepy, **5a**; 4-Mepy, **5b**; 2-Brpy, **5c**) was filtered off. Finally, the dinuclear alkylidene complexes **5** were dissolved in methylene chloride (3 mL) and layered with diethyl ether (10 mL). After 2 days yellow, air-sensitive crystals of **5** were filtered, washed with diethyl ether (5 mL), and dried in vacuo. Due to the spectroscopic data, it became evident that two isomers (*syn*, *anti*) were formed.

***trans*-[{PtCl(2-Mepy)}$_2${*μ*-C(OBu)Me}$_2$] (5a).** Yield: 87 mg (68%). T_{dec}: 145−147 °C. Anal. Found: C, 34.06; H, 4.73; N, 3.44. $C_{24}H_{38}Cl_2N_2O_2Pt_2$ (847.63) requires: C, 34.01; H, 4.52; N, 3.30. ^{1}H NMR (400 MHz, CD$_2$Cl$_2$): *δ* 0.98 (t, ^3J(H,H) = 7.21 Hz, 6H, C*H*$_3$, Bu), 1.47 (m, 4H, *γ*-C*H*$_2$), 1.81 (m, 4H, *β*-C*H*$_2$), 1.83/1.92 (s+d, ^3J(Pt,H) = 18.26/19.09 Hz, 4.5H/1.5H, C*H*$_3$), 2.92 (s, 6H, C*H*$_3$, 2-Mepy), 4.33 (m, 4H, α-C*H*$_2$), 7.39 (m, 4H, *H*3, *H*5), 7.81 (m, 2H, *H*4), 8.25 (m, 2H, *H*6). ^{13}C NMR (100 MHz, CD$_2$Cl$_2$): *δ* 14.0 (s, *C*H$_3$, Bu), 19.8 (s, *γ*-*C*H$_2$), 25.5 (s, *C*H$_3$, 2-Mepy), 31.5/31.7 (s, *β*-*C*H$_2$), 39.9/40.5 (s(br), *C*H$_3$), 73.7/74.3 (s(br), α-*C*H$_2$), 122.1/123.3 (s, *C*5), 126.4/127.5 (s, *C*3), 138.0/138.2 (s, *C*4), 150.0/150.7 (s, *C*6), 159.6/159.9 (s, *C*2), 182.2/182.6 (s+d, ^1J(Pt,C) = 635.9/638.4 Hz, $C_{carbene}$). ^{195}Pt NMR (107 MHz, CD$_2$Cl$_2$): *δ* −4737/−4815 (m). IR: *ν* 3072(w), 2953(s), 2904(s), 2866(s), 1604(m), 1462(s), 1377(w), 1348(w), 1292(w), 1259(w), 1186(s), 1134(s), 1099(s), 1065(s), 1026(s), 920(m), 802(m), 762(s), 621(s) cm^{-1}.

***trans*-[{PtCl(4-Mepy)}$_2${*μ*-C(OBu)Me}$_2$] (5b).** Yield: 65 mg (51%). T_{dec}: 134−138 °C. Anal. Found: C, 33.96; H, 4.49; N, 3.35. $C_{24}H_{38}Cl_2N_2O_2Pt_2$ (847.63) requires: C, 34.01; H, 4.52; N, 3.30. ^{1}H NMR (400 MHz, CD$_2$Cl$_2$): *δ* 0.96 (t, ^3J(H,H) = 7.47 Hz, 6H, C*H*$_3$, Bu), 1.42 (q, ^3J(H,H) = 7.19 Hz, 4H, *γ*-C*H*$_2$), 1.74 (m, 4H, *β*-C*H*$_2$), 1.90 (s+d, ^3J(Pt,H) = 19.92 Hz, 6H, C*H*$_3$), 2.45 (s, 6H, C*H*$_3$, 4-Mepy), 4.29 (m, 4H, α-C*H*$_2$), 7.32 (m, 4H, *m*-C*H*), 8.41 (m, 4H, *o*-C*H*). ^{13}C NMR (50 MHz, CD$_2$Cl$_2$): *δ* 14.0 (s, *C*H$_3$, Bu), 19.8 (s, *γ*-*C*H$_2$), 21.1 (s, *C*H$_3$, 4-Mepy), 31.6 (s, *β*-*C*H$_2$), 39.7/40.4 (s+d, ^2J(Pt,C) = 58.0/48.8 Hz, *C*H$_3$), 74.4 (s+d, ^3J(Pt,C) = 39.7 Hz, α-*C*H$_2$), 126.7 (s(br), *m*-*C*H), 150.2/150.3 (s, *o*-*C*H), 151.0 (s(br), *p*-*C*), 182.1/183.4 (s, $C_{carbene}$). ^{195}Pt NMR (107 MHz, CD$_2$Cl$_2$): *δ* −4738/−4730 (m). IR: *ν* 3043(w), 2954(s), 2908(s), 2866(s), 1618(s), 1498(w), 1456(m), 1433(m), 1350(w), 1184(m), 1136(s), 1101(s), 1066(m), 1024(s), 980(m), 920(m), 812(s), 733(w), 623(s) cm^{-1}.

***trans*-[{PtCl(2-Brpy)}$_2${*μ*-C(OBu)Me}$_2$] (5c).** Yield: 135 mg (92%). T_{dec}: 131 °C. Anal. Found: C, 26.24; H, 3.51; N, 2.61. $C_{22}H_{32}Br_2Cl_2N_2O_2Pt_2$ (977.37) requires: C, 27.04; H, 3.30; N, 2.87. ^{1}H NMR (200 MHz, CD$_2$Cl$_2$): *δ* 0.96 (t, ^3J(H,H) = 7.32 Hz, 6H, C*H*$_3$, Bu), 1.43 (m, 4H, *γ*-C*H*$_2$), 1.76 (m, 4H, *β*-C*H*$_2$), 2.10/2.30 (s(br), 1.5H/4.5H, C*H*$_3$), 4.32 (m, 4H, α-C*H*$_2$), 7.34 (m, 2H, *H*5), 7.60 (m, 4H, *H*3, *H*4), 8.33 (m, 2H, *H*6). ^{13}C NMR (50 MHz, CD$_2$Cl$_2$): *δ* 14.0 (s(br), *C*H$_3$, Bu), 19.8 (s(br), *γ*-*C*H$_2$), 31.6 (s(br), *β*-*C*H$_2$), 42.4 (s(br), *C*H$_3$), 74.7 (s(br), α-*C*H$_2$), 123.9 (s, *C*5), 128.6 (s, *C*3), 138.8 (s, *C*4), 142.6 (s, *C*2), 150.6 (s, *C*6). The carbene C atoms were not observed. IR: *ν* 3076(w), 2951(s), 2904(s), 2864(s), 1585(m), 1556(w), 1452(m), 1419(m), 1352(w), 1186(m), 1132(s), 1024(s), 979(m), 922(w), 762(s), 621(s) cm^{-1}.

3.5. Reactivity of Complex 3 toward Monodentate Phosphines. To a suspension of **3** (100 mg, 0.15 mmol) in methylene chloride (3 mL) was added a solution of the corresponding monodentate phosphine L (L = PPh$_3$, PPh$_2$(4-py); 0.30 mmol) in methylene chloride (1 mL) with stirring at −70 °C. Within 2 min a brownish-yellow solution was formed. To this reaction mixture was slowly added diethyl ether (10 mL), and the resulting solution was stored at −40 °C. After 2 days yellow, air-sensitive crystals of *trans*-[{PtCl(L)}$_2${*μ*-C(OBu)Me}$_2$] (L = PPh$_3$, **6a**; PPh$_2$(4-py), **6b**) were filtered, washed with diethyl ether (2 mL), and dried in vacuo. Due to the spectroscopic data, it became evident that two isomers (*syn*, *anti*) were formed.

***trans*-[{PtCl(PPh$_3$)}$_2${*μ*-C(OBu)Me}$_2$] (6a).** Yield: 135 mg (75%). T_{dec}: 140 °C. Anal. Found: C, 47.30; H, 4.64; Cl, 6.37. $C_{48}H_{54}Cl_2O_2P_2Pt_2$ (1185.95) requires: C, 48.61; H, 4.59; Cl, 5.98. ^{1}H NMR (200 MHz, CD$_2$Cl$_2$): *δ* 0.79/0.85 (t, ^3J(H,H) = 7.37/7.37 Hz, 4.5H/1.5H, C*H*$_3$, Bu), 1.22−1.65 (m, 8H, *β*-, *γ*-C*H*$_2$), 1.90/2.09 (m, 1.5H/4.5H, C*H*$_3$), 3.68 (m, 1.5H, H$_a$, α-C*H*$_2$), 3.80 (m, 0.5H, H$_a$, α-C*H*$_2$), 4.29 (m, 1.5H, H$_b$, α-C*H*$_2$), 4.41 (m, 0.5H, H$_b$, α-C*H*$_2$), 7.37 (m, 18H, *o*-, *p*-C*H*), 7.58 (m, 12H, *m*-C*H*). ^{13}C NMR (100 MHz, CD$_2$Cl$_2$): *δ* 13.7 (s(br), *C*H$_3$, Bu), 19.4/19.5 (s, *γ*-*C*H$_2$), 30.4/30.6 (s, *β*-*C*H$_2$), 38.9/39.6 (m, *C*H$_3$), 75.4/75.8 (m, α-*C*H$_2$), 127.4/128.4 (m, *m*-*C*H), 129.8/130.3 (m, *i*-*C*), 130.1/131.1 (s, *p*-*C*H), 135.0/135.5 (m, *o*-*C*H), 201.5/202.1 (s, $C_{carbene}$). ^{31}P NMR (81 MHz, CD$_2$Cl$_2$): *δ* 28.2/29.6 (m, ^1J(Pt,Pt) = 5680/5900 Hz, ^1J(Pt,P) = 3854/3848 Hz, ^2J(Pt,P) = 328/326 Hz, ^3J(P,P) = 21/18 Hz). ^{195}Pt NMR (107 MHz, CD$_2$Cl$_2$): *δ* −4863/−4848 (m). IR: *ν* 3054(w), 2958(m), 2928(m), 2856(m), 1480(m), 1434(s), 1146(s), 1098(s), 1008(s), 750(m), 510(s) cm^{-1}.

***trans*-[{PtCl{PPh$_2$(4-py)}}$_2${*μ*-C(OBu)Me}$_2$] (6b).** Yield: 160 mg (89%). T_{dec}: 122−127 °C. Anal. Found: C, 46.56; H, 4.80; N, 2.51. $C_{46}H_{52}Cl_2N_2O_2P_2Pt_2$ (1187.93) requires: C, 46.51; H, 4.41; N, 2.36. ^{1}H NMR (200 MHz, CD$_2$Cl$_2$): *δ* 0.83 (m, 6H, C*H*$_3$, Bu), 1.21−1.73 (m, 8H, *β*-, *γ*-C*H*$_2$), 1.96/2.14 (m, 1.5H/4.5H, C*H*$_3$), 3.63 (m, 1.5H, H$_a$, α-C*H*$_2$), 3.76 (m, 0.5H, H$_a$, α-C*H*$_2$), 4.22 (m, 1.5H, H$_b$, α-C*H*$_2$), 4.36 (m, 0.5H, H$_b$, α-C*H*$_2$), 7.30−7.72 (m, 24H, *o*-, *m*-, *p*-C*H*, Ph, *m*-C*H*, 4-py), 8.61 (m, 4H, *o*-C*H*, 4-py). ^{13}C NMR (100 MHz, CD$_2$Cl$_2$): *δ* 14.1 (s, *C*H$_3$, Bu), 19.7/19.8 (s, *γ*-*C*H$_2$), 30.7/30.8 (s, *β*-*C*H$_2$), 39.6/40.2 (m, *C*H$_3$), 76.0/76.3 (m, α-*C*H$_2$), 128.4 (“t”, *N* = 10.7 Hz, *m*-*C*H, 4-py), 128.6 (“t”, *N* = 10.7 Hz, *m*-*C*H, Ph), 130.4 (m, *i*-*C*, Ph), 131.4 (s, *p*-*C*H, Ph), 135.5 (m, *o*-*C*H, Ph), 141.8 (“t”, *N* = 48.3 Hz, *i*-*C*, 4-py), 149.4 (m, *o*-*C*H, 4-py), 200.8 (s, $C_{carbene}$). ^{31}P NMR (81 MHz, CD$_2$Cl$_2$): *δ* 26.6/28.1 (m, ^1J(Pt,Pt) = 5830/6050 Hz, ^1J(Pt,P) = 3797/3805 Hz, ^2J(Pt,P) = 336/331 Hz, ^3J(P,P) = 23/18 Hz). ^{195}Pt NMR (107 MHz, CD$_2$Cl$_2$):

Table 5. Crystallographic and Data Collection Parameters for Complexes 5a, 5b, and 5c

	5a	**5b**	**5c**
empirical formula	$C_{24}H_{38}Cl_2N_2O_2Pt_2$	$C_{24}H_{38}Cl_2N_2O_2Pt_2$	$C_{22}H_{32}Br_2Cl_2N_2O_2Pt_2$
M_r/g·mol^{-1}	847.64	847.64	977.40
cryst size/mm	0.34 × 0.11 × 0.10	0.45 × 0.27 × 0.22	0.20 × 0.20 × 0.11
cryst syst	monoclinic	monoclinic	triclinic
space group	$P2_1/c$	$P2_1/n$	$P\bar{1}$
a/Å	8.570(2)	8.388(3)	8.368(3)
b/Å	14.353(3)	19.260(4)	8.452(3)
c/Å	12.100(3)	9.073(3)	10.835(3)
α/deg	90	90	103.28(3)
β/deg	105.23(3)	112.84(3)	92.23(3)
γ/deg	90	90	113.92(3)
V/Å^3	1436.1(6)	1350.8(7)	674.2(4)
Z	2	2	1
D_{calc}/g·cm^{-1}	1.960	2.084	2.407
μ(Mo Kα)/mm^{-1}	9.938	10.565	13.547
F(000)	804	804	454
θ range/deg	3.33−35.00	3.23−30.00	3.31−28.00
no. of reflns collected	21 962	22 537	8957
no. of reflns obsd [$I > 2\sigma(I)$]	6246	3868	3204
no. of reflns indep	4609	3607	2995
no. of data/params/restraints	6246/148/0	3868/155/3	3204/145/0
goodness-of-fit on F^2	1.073	1.078	1.028
R_1 (Σ)/R_1 ($I > 2\sigma(I)$)	0.0626/0.0390	0.0280/0.0246	0.0270/0.0249
wR_2 (Σ)/wR_2 ($I > 2\sigma(I)$)	0.0927/0.0881	0.0574/0.0562	0.0632/0.0625
largest diff peak and hole/e·Å^{-3}	4.510/−2.459	2.439/−2.230	1.751/−1.624
T_{min}/T_{max}	0.135/0.414	0.087/0.205	0.064/0.264

δ −4875/−4860 (m). IR: ν 3055(w), 2953(m), 2864(m), 1574(m), 1434(m), 1398(m), 1153(s), 1097(s), 1009(s), 744(m), 694(s), 510(s) cm^{-1}.

3.6. Reactivity of Complex 3 toward Tetrahydrothiophene. To a suspension of **3** (100 mg, 0.15 mmol) in methylene chloride (1 mL) was added tetrahydrothiophene (26.5 mg, 0.30 mmol) with stirring at −70 °C. Immediately a yellow solution was formed. Then *n*-pentane (10 mL) was added, and the resulting solution was stored at −40 °C. After 2 days yellow, air-sensitive crystals of *trans*-[{PtCl(tht)}$_2${μ-C(OBu)Me}$_2$] (**7**) were filtered, washed with *n*-pentane (2 mL) at −40 °C, and dried in vacuo. Due to the spectroscopic data, it became evident that two isomers (*syn*, *anti*) were formed.

Yield: 78 mg (58%). T_{dec}: 117 °C. Anal. Found: C, 28.59; H, 4.79; N, 7.69. $C_{20}H_{40}Cl_2O_2Pt_2S_2$ (837.72) requires: C, 28.67; H, 4.81; N, 7.66. ^{1}H NMR (200 MHz, CD$_2$Cl$_2$): δ 0.89 (t, ^3J(H,H) = 7.06 Hz, 6H, CH_3, Bu), 1.37 (m, 4H, γ-CH_2), 1.63 (m, 4H, β-CH_2), 2.15 (s+d, ^3J(Pt,H) = 6.64 Hz, 6H, CH_3), 2.29 (s(br), 8H, β-CH_2, tht), 3.35 (s(br), 8H, α-CH_2, tht), 3.86 (s(br), 2H, H$_a$, α-CH_2), 4.02 (s(br), 2H, H$_b$, α-CH_2). ^{13}C NMR (50 MHz, CD$_2$Cl$_2$): δ 14.0 (s, CH$_3$, Bu), 19.8 (s, γ-CH$_2$), 30.9 (s, β-CH$_2$, tht), 31.6 (s, β-CH$_2$), 37.1 (s, α-CH$_2$, tht), 40.5 (s(br), CH$_3$), 75.3 (s(br), α-CH$_2$), 191.0/200.6 (s, $C_{carbene}$). ^{195}Pt NMR (107 MHz, CD$_2$Cl$_2$): δ −4783/−4882 (m). IR: ν 2943(s), 2864(s), 1456(m), 1429(m), 1348(m), 1261(m), 1178(s), 1142(s), 1097(s), 1065(s), 1020(s), 976(s), 922(m), 881(w), 831(w), 669(w), 609(s) cm^{-1}.

Table 6. Crystallographic and Data Collection Parameters for Complexes 6a·2CHCl$_3$ and 6b·2CHCl$_3$

	6a·2CHCl$_3$	**6b**·2CHCl$_3$
empirical formula	$C_{50}H_{56}Cl_8O_2P_2Pt_2$	$C_{24}H_{27}Cl_4NOPPt$
M_r/g·mol^{-1}	1424.67	713.33
cryst size/mm	0.20 × 0.20 × 0.10	0.20 × 0.10 × 0.05
cryst syst	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
a/Å	9.986(3)	9.905(1)
b/Å	12.136(2)	10.767(3)
c/Å	13.073(2)	13.881(4)
α/deg	62.41(2)	87.27(2)
β/deg	73.73(2)	82.49(2)
γ/deg	67.48(2)	66.80(2)
V/Å^3	1286.8(5)	1348.8(5)
Z	1	2
D_{calc}/g·cm^{-1}	1.838	1.756
μ(Mo Kα)/mm^{-1}	5.946	5.674
F(000)	694	694
θ range/deg	1.77−25.00	2.84−26.00
no. of reflns collected	5278	22 411
no. of reflns obsd [$I > 2\sigma(I)$]	4519	5253
no. of reflns indep	4029	4369
no. of data/params/restraints	4519/290/0	5253/308/1
goodness-of-fit on F^2	1.038	1.051
R_1 (Σ)/R_1 ($I > 2\sigma(I)$)	0.0511/0.0420	0.0549/0.0416
wR_2 (Σ)/wR_2 ($I > 2\sigma(I)$)	0.1327/0.1187	0.1085/0.1041
largest diff peak and hole/e·Å^{-3}	2.234/−2.049	2.721/−1.264
T_{min}/T_{max}	0.541/0.997	0.653/1.000

3.7. X-ray Crystal Structure Determinations. Intensity data were collected on STOE-IPDS and KUMA KM4 CCD diffractometers using graphite-monochromatized Mo Kα radiation (λ = 0.71073 Å) at 100(2) K (**5a**−**c**, **6b**·2CHCl$_3$) and 200(2) K, respectively. A summary of the crystallographic data, the data collection parameters, and the refinement parameters is given in Tables 5 and 6. In all structures the absorption corrections were applied semiempirically. The structures were solved by direct methods with SHELXS-97 and refined using full-matrix least-squares routines against F^2 with SHELXL-97.[23] All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were refined isotropically and included in the models in calculated positions using the riding model. In **6b**·2CHCl$_3$ the atoms C5 and C6 were found to be disordered over two positions (C5/C5A and C6/C6A). The occupation factors of 0.41 (C5, C6) and 0.59 (C5A, C6A) were calculated during the refinement process. Crystallographic data for the structures reported in this paper have been deposited at the Cambridge Crystallographic Data Center (CCDC) as Supplementary Publication No. CCDC-664395 (**5a**), CCDC-664396 (**5b**), CCDC-664397 (**5c**), CCDC-664398 (**6a**·2CHCl$_3$), and CCDC-664399 (**6b**·2CHCl$_3$). Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge, CB2 1EZ, U.K. (fax (internat.) +44-1223-336033; e-mail deposit@ccdc.cam.ac.uk).

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3.8. Computational Details. The DFT calculations were performed by employing the Gaussian03 program package[24] using the B3LYP functional.[25] For the main group atoms the basis set 6-311+G(d,p) was employed as implemented in the program. A triple-ζ valence basis set was used for Pt with polarization functions added (TZVPP) as provided by Ahlrichs and co-workers.[26] For its core orbitals an effective core potential with consideration of relativistic effects was used.[27] The QTAIM analysis and the visualization were performed using the program package AIMPAC as provided by Bader et al.[28] Complex **6a′** was optimized in C_i symmetry. The resulting geometries were characterized as equilibrium structures by the analysis of the force constants of normal vibrations.

Acknowledgment. We gratefully acknowledge support by the Deutsche Forschungsgemeinschaft. We also thank Merck (Darmstadt, Germany) for gifts of chemicals.

Supporting Information Available: CIFs giving X-ray crystallographic data and Cartesian coordinates of atom positions calculated for structure **6a′**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM7007138

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