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Reactivity of Platina-β-diketones with 1,4-Diazabuta-1,3-dienes: Synthesis and Characterization of Acylplatinum(II) Complexes with RN═CMeCMe═NR and RN(H)CH═CHN(R)C(O)Me Ligands

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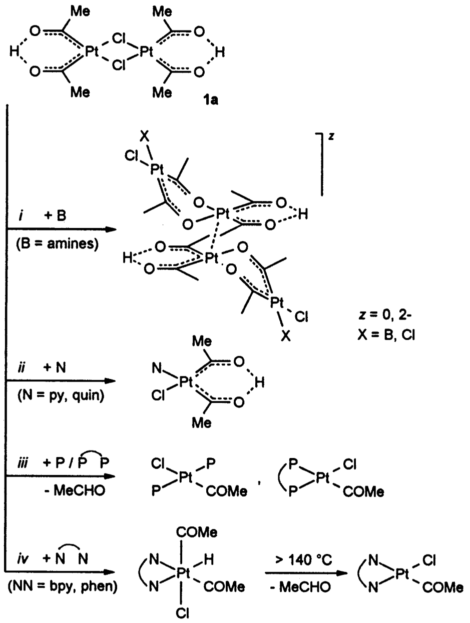
The dinuclear platina-β-diketone $[Pt_2\{(COMe)_2H\}_2(\mu\text{-}Cl)_2]$ (**1a**) reacts with 2,3-dimethyl-substituted 1,4-diazabuta-1,3-dienes RN═CMeCMe═NR (R = *n*-Pr, Ph), yielding the acylplatinum(II) complexes [Pt(COMe)$_2$\{(*n*-Pr)N═CMeCMe═N(*n*-Pr)\}] (**2a**) and [Pt(COMe)Cl(PhN═CMeCMe═NPh)] (**2b**), respectively. Constitutions of these complexes were confirmed by ^{1}H and ^{13}C NMR spectroscopy and by single-crystal X-ray diffraction analyses. In these reactions the acyl(hydrido)platinum(IV) complexes [Pt(COMe)$_2$Cl(H)(RN═CMeCMe═NR)] (**3a**, R = *n*-Pr; **3b**, R = Ph) were detected (^{1}H NMR spectroscopy) as intermediates, from which complexes **2a**,**b** were formed by reductive elimination of HCl and MeCHO, respectively. Reactions of the platina-β-diketone **1a** with diazadiene ligands that are unsubstituted at the 2- and 3-positions, RN═CHCH═NR (R = *n*-Pr, *i*-Pr, *c*-Hex, *t*-Bu), afforded platinum(II) complexes of the type [Pt(COMe)Cl\{RN(H)CH═CHN(R)C(O)Me\}] (**4a**, R = *n*-Pr; **4b**, R = *i*-Pr; **4c**, R = *c*-Hex; **4d**, R = *t*-Bu). All complexes were characterized by NMR spectroscopy (^{1}H, ^{13}C), and the structure of complex **4d** was determined by single-crystal X-ray diffraction as well. The organo ligand is formally obtained by 1,4-addition of MeC(O)−H to the diazadiene ligand RN═CHCH═NR. On the basis of DFT calculations of the model complex [Pt(COMe)Cl\{MeN(H)CH═CHN(Me)C(O)Me\}] (**6**) and of the (relaxed) free ligand MeN(H)CH═CHN(Me)C(O)Me (**7**) the electronic structure of complex **6** and the bonding mode of ligand **7** is discussed. DFT calculation of the isomeric acyl(hydrido)platinum(IV) complex [Pt(COMe)$_2$Cl(H)(MeN═CHCH═NMe)] (**9a**) indicated that it is 18.2 kcal/mol higher in energy than complex **6**. Thus, **9a** may be an intermediate in the formation of complex **6**.

Introduction

Reactions of hexachloroplatinic acid in butanol with the alkynylsilanes R′C≡CSiMe$_3$ afforded the dinuclear platina-β-diketones $[Pt_2\{(COR)_2H\}_2(\mu\text{-}Cl)_2]$ (**1**; R = R′ + CH$_2$) via Zeise's acid with a butene ligand, H[PtCl$_3$(η^2-CH$_2$═CHEt)], as intermediate.[1] Complexes **1** have only 16 valence electrons and are kinetically labile complexes, in contrast to the electronically saturated (18 ve) and kinetically inert Lukehart metalla-β-diketones [M\{(COR)$_2$H\}L$_x$] (M = Mn, Re, Fe, ...) with carbonyl and/or cyclopentadienyl coligands L.[2] Platina-β-diketones **1** exhibit unique reactivity. The methyl-substituted complex **1a** (R = Me) reacts (Scheme 1) (i) with amines and other bases, yielding platina-β-diketonates of platina-β-diketones that can be regarded as organometallic analogues of platinum blues,[3] (ii) with pyridines and quinoline, yielding mononuclear platina-β-diketones,[4] and (iii) with phosphines and diphosphines, yielding acylplatinum(II) complexes with cleavage of acetaldehyde.[4] Reactions (iv) with bipyridines and phenanthrolines resulted in formation of hydrido(acetyl)platinum(IV) complexes that exhibited an astonishing

Scheme 1



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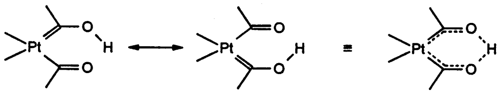
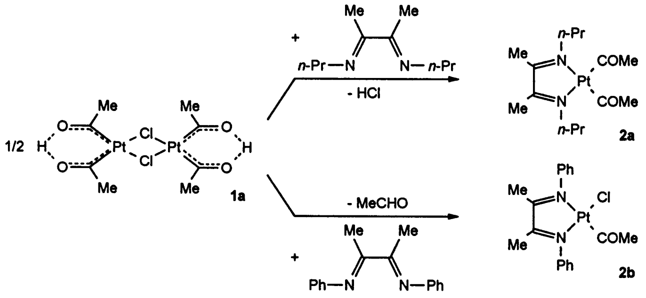
Scheme 2



Scheme 3



thermal stability. Only at temperatures above 140 °C did the solids undergo a reductive elimination of acetaldehyde, yielding acetylplatinum(II) complexes.[5] Major aspects of the reactivity of platina-β-diketones can be understood when they are regarded as hydroxycarbene complexes that are intramolecularly stabilized by a hydrogen bridge to an acyl ligand (Scheme 2).

Here we report on reactions of the platina-β-diketone **1a** with 1,4-diazabuta-1,3-diene (dab) ligands. These ligands have attracted interest mainly for two reasons. (i) Compared with bipyridines and phenanthrolines, the most widely used ligands with $-N{=}CC{=}N-$ skeletons, they are better π-acceptors. (ii) Because dab ligands may π-coordinate through nitrogen lone pairs and π-coordinate through C=N bonds, they exhibit versatile coordination modes ranging from 2-electron up to 8-electron donors. Due to a pronounced dependence of the reactivity of platina-β-diketone on the electronic properties of ligands, new reactions could be expected to be found using dab ligands. This will be shown in reactions of the platina-β-diketone **1a** with 1,4-disubstituted dab ligands RN=CR′CR′=NR being 2,3-dimethyl-substituted (R′ = Me; R = *n*-Pr, Ph) on the one side and unsubstituted at the 2- and 3-positions (R′ = H; R = *n*-Pr, *i*-Pr, *c*-Hex, *t*-Bu) on the other side.

Results and Discussion

Synthesis and Characterization of the Complexes [Pt(COMe)$_2${(*n*-Pr)N=CMeCMe=N(*n*-Pr)}] (2a) and [Pt(COMe)Cl(PhN=CMeCMe=NPh)] (2b). (a) Synthesis. The platina-β-diketone **1a** reacted with dab ligands (*n*-Pr)N=CMeCMe=N(*n*-Pr) and PhN=CMeCMe=NPh in thf solution at −40 °C, yielding the acylplatinum(II) complexes [Pt(COMe)$_2${(*n*-Pr)N=CMeCMe=N(*n*-Pr)}] (**2a**) and [Pt(COMe)Cl(PhN=CMeCMe=NPh)] (**2b**), respectively (Scheme 3). The acylplatinum(II) complexes **2a**,**b** were isolated at room temperature in moderate yields (40% in both cases) as yellow microcrystalline substances. Both complexes were quite soluble in most organic solvents, excluding diethyl ether and hydrocarbon solvents. In the solid state they were stable in air for several days; however, in solution slow decomposition took place within 1 day.

When isolation of complexes was carried out at temperatures around 0 °C, mixtures of several substances were isolated, usually containing complexes **2a**,**b** as main components. However, in all experiments small amounts of acyl(hydrido)platinum(IV) complexes of the type [Pt(COMe)$_2$Cl(H)(RN=CMeCMe=NR)] (**3a**, R = *n*-Pr; **3b**, R = Ph) were clearly detected in ^{1}H NMR spectra by strongly high field shifted signals of hydrido ligands (**3a**, $\delta(^1H)$ −18.34 ppm, $^1J_{Pt,H} = 1476.9$ Hz; **3b**, $\delta(^1H)$ −19.26 ppm, $^1J_{Pt,H} = 1576.7$ Hz). In an individual case, complex **3b** was even obtained as the main product (^{1}H NMR: COCH_3, δ 2.25/2.45 ppm, $^3J_{Pt,H}$ 37.4/18.3 Hz; dab (CH_3), δ 2.30/2.32 ppm). Most likely, these complexes **3** are intermediates that undergo reductive elimination of HCl (yielding **2a**) or MeCHO (yielding **2b**). Analogous reactions of platina-β-diketone **1a** with bipyridines and phenanthrolines ($N^\frown N$) afforded acyl(hydrido)platinum(IV) complexes of type **3**, [Pt(COMe)$_2$Cl(H)($N^\frown N$)], which are thermally stable and undergo reductive elimination of MeCHO only at elevated temperature (cf. Scheme 1, iv).

In contrast to RN=CMeCMe=NR (R = *n*-Pr, Ph), the tetraphenyl-substituted dab ligand PhN=CPhCPh=NPh did not react with the platina-β-diketone **1a** at all. Most likely, this is due to the *Z*−gauche−*Z* conformation of free PhN=CPhCPh=NPh.[6] Thus, coordination as an *N*,*N*-chelating ligand requires not only rotation around the central C−C bond but also rearrangement of *N*-bound phenyl groups.

(b) Spectroscopic Investigations. Complexes **2a**,**b** were fully characterized by single-crystal X-ray diffraction analyses and by ^{1}H and ^{13}C NMR spectroscopy. In complex **2a** the two acetyl groups ($\delta(^1H_{Me})$ 2.17 ppm, $\delta(^{13}C_{Me})$ 43.6 ppm, $\delta(^{13}C_{CO})$ 231.6 ppm) are chemically equivalent. Resonances of the acetyl ligand in complex **2b** are similar ($\delta(^1H_{Me})$ 2.13 ppm, $\delta(^{13}C_{Me})$ 39.7 ppm, $\delta(^{13}C_{CO})$ 213.8 ppm) to those of complex **2a**. In comparison with the free ligand RN=CMeCMe=NR ligand the methyl H atoms in complex **2a** (R = *n*-Pr) are slightly low field shifted (0.07 ppm), whereas those in complex **2b** (R = Ph) are strongly high field shifted by 0.54 and 0.28 ppm, respectively.

(c) Molecular Structures. Single crystals of complexes **2a**,**b** suitable for X-ray diffraction analyses were grown from CDCl$_3$ solution in NMR tubes. Molecular structures of complexes **2a**,**b** are shown in Figures 1 and 2 and selected bond lengths and angles in Tables 1 and 2, respectively. Both complexes crystallize as discrete molecules; there are no unusual intermolecular contacts. Complex **2b** crystallizes with one molecule of CDCl$_3$. The platinum centers are nearly planar, tetracoordinated by a dab ligand and two acetyl ligands in **2a** and by a dab ligand, one chloro ligand, and one acetyl ligand in **2b**. Within the experimental error (3σ criterion), there are no significant differences in the geometrical parameters between the two acetyl ligands either in **2a** (mean values: Pt−C 2.00 Å, C−O 1.22 Å, C−C 1.49 Å; all angles between 118.0(4) and 121.9(3)°), or in complex

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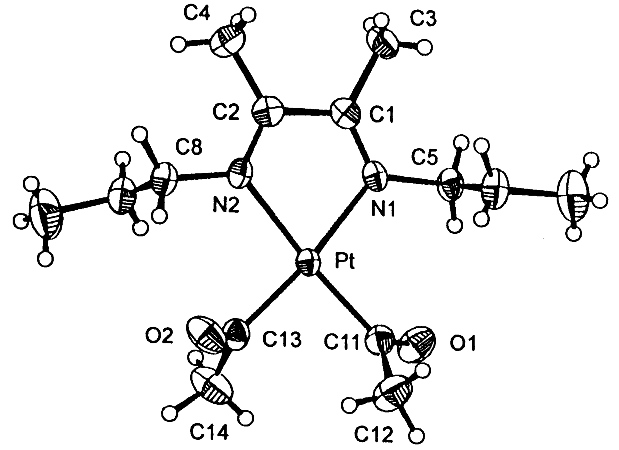

Figure 1. Molecular structure of [Pt(COMe)$_2${(*n*-Pr)N=CMeCMe=N(*n*-Pr)}] (**2a**) showing atom numbering (displacement ellipsoids at 50% probability).

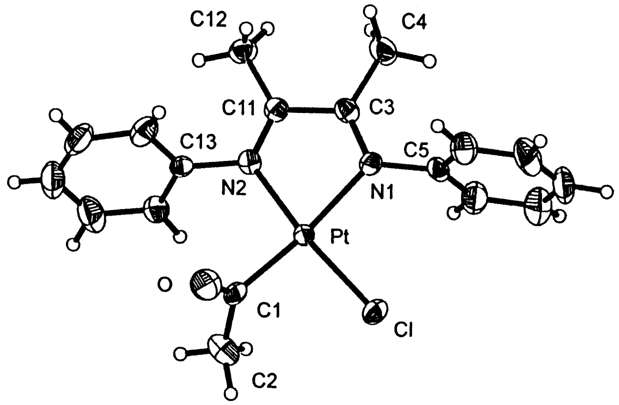

Figure 2. Molecular structure of [Pt(COMe)Cl(PhN=CMeCMe=NPh)]·CDCl$_3$ (**2b**·CDCl$_3$) showing atom numbering (displacement ellipsoids at 50% probability). The CDCl$_3$ molecule is not shown for clarity.

Table 1. Selected Interatomic Distances (in Å), Angles (in deg), and Torsion Angles (in deg) for 2a

Pt–N1	2.123(3)	N2–C2	1.288(4)
Pt–N2	2.113(3)	C1–C2	1.484(6)
Pt–C11	2.003(4)	C11–O1	1.215(5)
Pt–C13	1.995(3)	C13–O2	1.227(5)
N1–C1	1.282(5)		
N1–Pt–N2	76.0(1)	Pt–C11–O1	121.7(3)
N1–Pt–C11	98.2(1)	Pt–C13–O2	121.9(3)
N2–Pt–C13	96.9(1)	Pt–N1–C1	115.7(3)
C11–Pt–C13	88.8(2)	Pt–N2–C2	116.2(3)
N1–Pt–C13	172.9(1)	N1–C1–C2	116.4(3)
N2–Pt–C11	174.2(1)	N2–C2–C1	115.4(3)
N1–C1–C2–N2	6.4(4)		

2b (Pt–C 2.014(6) Å, C–O 1.188(8) Å, C–C 1.50(1) Å; angles between 117.4(5) and 121.8(6)°). In complex **2a** the two oxygen atoms of cis acetyl ligands are on opposite sites of the coordination plane, obviously, to minimize the electrostatic repulsion between the oxygen atoms (O1–C11···C13–O2 173.6(4)°). The plane of the acetyl ligand in **2b** includes an angle of 72.8(3)° with the coordination plane.

Synthesis and Characterization of Complexes [Pt(COMe)Cl{RN(H)CH=CHN(R)C(O)Me}] (4a–d).

(a) Synthesis. The platina-β-diketone **1a** reacted with dab ligands RN=CHCH=NR (R = *n*-Pr, *i*-Pr, *c*-Hex, *t*-Bu) at −40 °C in thf solution, yielding the platinum(II) complexes [Pt(COMe)Cl{RN(H)CH=CHN(R)C(O)Me}] (**4a**, R = *n*-Pr; **4b**, R = *i*-Pr; **4c**, R = *c*-Hex; **4d**, R = *t*-Bu) (Scheme 4). Complexes **4a–d** were isolated as white microcrystalline substances with moderate to good yields (**4a**, 45%; **4b**, 88%; **4c**, 84%; **4d**, 61%) that are very soluble in chlorinated solvents, less soluble in thf, and insoluble in diethyl ether and hydrocarbons. They are moderately stable toward air and moisture in the solid state. However, in chloroform and thf solutions a substantial decomposition over 24 h was observed. All complexes **4a–d** were fully characterized by means of ^{1}H and ^{13}C NMR spectroscopy and in the case of **4d** (R = *t*-Bu) also by X-ray structural analysis.

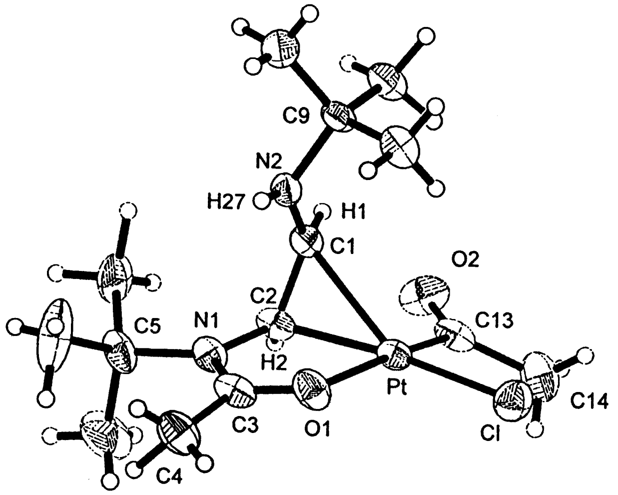

Figure 3. Molecular structure of [Pt(COMe)Cl{(*t*-Bu)N(H)CH=CHN(*t*-Bu)C(O)Me}] (**4d**) showing atom numbering (displacement ellipsoids at 50% probability).

Scheme 4

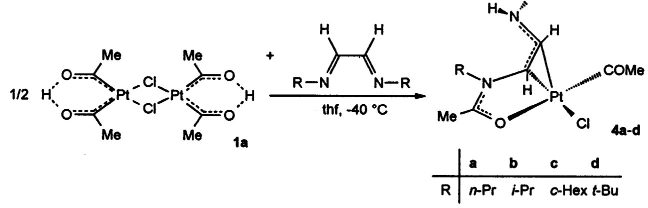

Table 2. Selected Interatomic Distances (in Å), Angles (in deg), and Torsion Angles (in deg) for 2b·CDCl$_3$

Pt–N1	2.137(5)	N1–C3	1.282(8)
Pt–N2	2.017(5)	N2–C11	1.295(8)
Pt–Cl	2.301(1)	C3–C11	1.507(7)
Pt–C1	2.014(6)	C1–O	1.188(8)
N1–Pt–N2	76.6(2)	Pt–C1–O	120.7(5)
N1–Pt–Cl	97.6(1)	Pt–C1–C2	117.4(5)
N2–Pt–C1	98.4(2)	Pt–N1–C3	115.1(3)
C1–Pt–Cl	87.5(2)	Pt–N2–C11	119.2(4)
N1–Pt–C1	173.6(2)	N1–C3–C11	114.8(5)
N2–Pt–Cl	174.1(1)	N2–C11–C3	114.3(5)
N1–C3–C11–N2	1.1(7)		

(b) Molecular Structure. Molecular structure of complex [Pt(COMe)Cl{(*t*-Bu)N(H)CH=CHN(*t*-Bu)C(O)Me}] (**4d**) is shown in Figure 3 along with the numbering scheme. Selected bond lengths and angles are given in Table 3. The complex crystallizes as discrete molecules; there are no unusual intermolecular contacts.

Table 3. Selected Interatomic Distances (in Å), Angles (in deg), and Torsion Angles (in deg) for 4d

Pt−C1	2.326(8)	C3−N1	1.33(1)
Pt−C2	2.057(9)	C3−O1	1.26(1)
Pt−C13	1.968(9)	C13−O2	1.22(1)
Pt−Cl	2.332(2)	C9−N2	1.48(1)
Pt−O1	2.147(6)	C5−N1	1.52(1)
C1−C2	1.43(1)	C3−C4	1.48(1)
C1−N2	1.33(1)	C13−C14	1.51(2)
C2−N1	1.45(1)		
C2−Pt−O1	76.7(3)	Pt−C2−N1	111.7(6)
C2−Pt−C13	96.1(4)	Pt−O1−C3	113.8(6)
C2−Pt−Cl	168.3(2)	Pt−C2−C1	81.6(5)
C13−Pt−Cl	95.4(3)	Pt−C1−N2	117.2(5)
C13−Pt−O1	169.2(3)	Pt−C13−O2	123.2(7)
O1−Pt−Cl	91.6(2)	Pt−C13−C14	118.7(7)
C1−Pt−C2	37.4(3)	C2−N1−C5	116.5(7)
C2−C1−N2	126.5(7)	C2−N1−C3	116.1(7)
C1−C2−N1	118.2(7)	N1−C3−O1	119.9(8)
C1−N2−C9	123.5(7)		
N1−C2−C1−N2	6(1)		

As can be seen in Figure 3, besides a chloro and an acetyl ligand, an enamine−amide type ligand, (*t*-Bu)N-(H)CH=CHN(*t*-Bu)C(O)Me, is coordinated to platinum. Platinum is essentially square planar coordinated by a chloro (Cl) and an acetyl ligand (C13) as well as by O1 and C2 of the organo ligand (angles between neighboring ligands 76.7(3)−96.1(4)°; sum of angles 359.8°). There is an additional weakly bound carbon atom (Pt−C1 2.326(8) Å). This distance is much longer than the Pt−C2 bond (2.057(9) Å). The Pt−C2 bond is rather short and Pt−C1 is rather long, as a comparison with Pt−C bond lengths in olefin platinum complexes (median 2.183 Å; lower/upper quartile 2.140/2.235 Å; 1484 observations[7]) reveals. Comparison of the Pt−O bond length in **4d** (2.147(6) Å) with those in other platinum complexes containing Pt−O=C moieties (median 2.029 Å; lower/upper quartile 2.009/2.049 Å; 221 observations[7]) reveals that the Pt−O1 bond is only a weak one. The five-membered Pt−O1−C3−N1−C2 cycle is best described as a half-chair twisted on Pt−O1.

The backbone of the dab ligand N1−C2−C1−N2 is twisted on the C1−C2 bond by 6(1)°. Both nitrogen atoms are essentially planar (sum of angles 359.5° (N1), 355.5° (N2)), indicating that they remained sp^2 hybridized. The σ-skeletons of N2 and those of the central carbon atoms C1 and C2 define a plane in a rough approximation (C9,N2,C1,C2,N1: maximum deviation from the plane 0.151(7) Å; back-bending of substituents on carbon atoms C1 and C2 when they are coordinated to Pt and strain due to the five-membered C2,N1,C3,O1,Pt ring may be the reason for relatively high deviations). Thus, π-electrons in the C2−C1−N2 unit may be delocalized. Furthermore, the σ-skeleton of N1 is part of a larger planar unit built up of the atoms C2−N1(C5)−C3(O1)−C4 (maximum deviation from the mean plane 0.047(8) Å). This arrangement allows a delocalization of π-electrons between O1−C3−N1. However, the two planes include an angle of 75.1(5)°, excluding any interactions of the two π systems.

In comparison with the noncomplexed *tert*-butyl-substituted diazadiene *t*BuN=CHCH=N*t*Bu (X-ray diffraction analysis of the *s-trans* conformer,[8] C−C 1.467(2)−1.477(2) Å, C=N 1.267(1)−1.269(2) Å; electron diffraction of the gauche conformer,[9] C−C 1.50(2) Å, C=N 1.283(6) Å), the C1−C2 bond in complex **4d** (1.43(1) Å) is slightly shorter. The C1=N2 bond (1.33(1) Å) which is not involved in the five-membered platinacycle is slightly longer, but it retains substantial double-bond character. On the other hand, the C2−N1 bond (1.45(1) Å) which is incorporated in the five-membered platinacycle is clearly a single bond.[10] The structural features of the C4,C3,O1,N1 unit correspond to those in carboxylic acid amides (**4d**, C3−N1 1.33(1) Å, C3=O1 1.26(1) Å; acyclic amides, C−N 1.342 Å, C=O 1.232 Å[10]).

(c) Spectroscopic Investigations. All complexes **4a−d** have similar ^{1}H and ^{13}C NMR spectroscopic signal patterns, showing that they belong to the same class of compounds. Selected data are summarized in Table 4. Assignments of signals in ^{1}H and ^{13}C NMR spectra were revealed by ^{1}H−^{1}H COSY and ^{1}H−^{13}C HETCOR NMR experiments. ^{1}H and ^{13}C chemical shifts of acetyl ligands in complexes **4** ($\delta(^1H_{CH_3})$ 2.25−2.30 ppm; $\delta(^{13}C_{CH_3})$ 41.5−42.8 ppm; $\delta(^{13}C_{CO})$ 201.1−204.1 ppm) are in the expected range as compared with other Pt(II) complexes of the type $[Pt(COMe)(Cl)L_2]$ ($L_2 = Ph_2P(CH_2)_nPPh_2$, $n = 2, 3$ (**5a**);[4] L_2 = 4,4′-R_2bpy, R = H, Me, *t*-Bu (**5b**);[5] L_2 = PhN=CMeCMe=NPh (**2b**)) reveals. In complexes **4** the $^2J_{Pt,C}$ coupling constants (138.4−152.2 Hz) are significantly larger than those in complexes **5** and **2b** (101.7−124.0 Hz). Analogously, the $^1J_{Pt,C}$ coupling constants in complexes **4** are larger than that in complex **5b** (R = H) (1072.4−1121.1 Hz vs 989 Hz). On the basis of the well-known dependence of the magnitudes of $^1J_{Pt,C}$ and $^2J_{Pt,C}$ coupling constants on trans influence,[11] this reflects a smaller trans influence of the oxygen donor in complexes **4** compared with the *N*- and *P*-donors in complexes **5** and **2b**.

In complexes **4** the two =CH− groups of the dab ligands are highly nonequivalent, exhibiting chemical shift differences $\Delta\delta(^1H)$ 2.00−2.73 ppm and $\Delta\delta(^{13}C)$ 68.6−103.6 ppm. The high-field-shifted N−*CH*= groups show a strong coupling to platinum ($^2J_{Pt,H}$ = 113.1 Hz (**4d**), 138.9 Hz (**4a**); $^1J_{Pt,C}$ = 393.7−480.5 Hz), whereas for the low-field-shifted NH−*CH*= groups platinum couplings were not observed. This can be understood on the basis that the molecular structure of **4d** shows a normal Pt−C2 bond length (2.057(9) Å), whereas the Pt−C1 distance is much longer (2.326(8) Å). Resonances of hydrogen atoms H bound to nitrogen are broad and were found between 4.3 ppm (**4d**) and 8.7 ppm (**4a**), exhibiting a strong dependence on the substituent R.

(d) DFT Calculations. To get an insight into the electronic structure of complex **4d**, DFT calculations were performed using the hybrid functional B3LYP and an effective core potential on platinum. Relativistic effects were considered. To save computational resources, *tert*-butyl substituents on nitrogen atoms in **4d**

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(7) Cambridge Structural Database (CSD); Cambridge Crystallographic Data Centre, University Chemical Laboratory, Cambridge, U.K.

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Table 4. Selected NMR Data (δ in ppm, J in Hz) for Complexes 4a−d

R	N*CH*=		NH*CH*=		N*H*	C(O)*CH*$_3$		*C*(O)
	δ_H ($^2J_{Pt,H}$)	δ_C ($^1J_{Pt,C}$)	δ_H	δ_C	δ_H	δ_H	δ_C ($^2J_{Pt,C}$)	δ_C ($^1J_{Pt,C}$)
n-Pr (**4a**)	4.92 (138.9)	53.7	7.5	157.3	8.7	2.25	42.8 (141.6)	204.1 (1121.1)
i-Pr (**4b**)	4.71	50.2 (480.5)	7.4[a]	143.6	7.3[a]	2.30	42.1 (147.5)	202.1 (1072.4)
c-Hex (**4c**)	4.76	51.7 (475.8)	7.1[a]	143.1	7.4[a]	2.30	42.1 (152.2)	202.0
t-Bu (**4d**)	5.04 (113.1)	59.2 (393.7)	7.0	127.8	4.3	2.29	41.5 (138.4)	201.1 (1075.1)

[a] The assignment may be reversed.

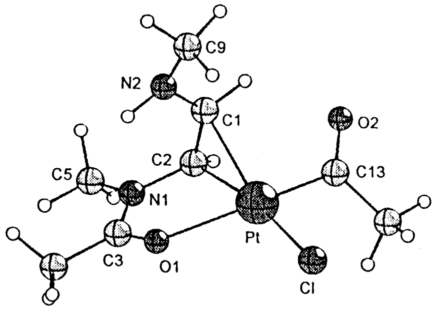

Figure 4. Calculated structure and numbering scheme of [Pt(COMe)Cl{MeN(H)CH=CHN(Me)C(O)Me}] (**6**).

were replaced by methyl substituents in the calculated complex **6**. Its structure is shown in Figure 4, and selected structural parameters are given in Table 5. The structure of complex **6** is close to that of complex **4d** (Table 5). The most important difference is the longer Pt−O1 bond in **6** compared with that in **4d** (Δ 0.211 Å). Furthermore, the calculated values for the stronger Pt−C2 bond and the weaker Pt−C1 bond are longer by 0.054 Å and shorter by 0.022 Å, respectively, than those in complex **4d**. Thus, the "asymmetry" of the olefin bonding C1−C2 in complex **4d** is greater than that in the calculated complex **6**. Inspection of NBO charges revealed that coordination of the ligand MeN(H)CH=CHN(Me)C(O)Me to the PtCl(COMe) moiety results in transfer of 0.186 electron.

Formal cleavage of the organo ligand of complex **6** and an optimization procedure resulted in a relaxed structure of the organo ligand MeN(H)CH=CHN(Me)C(O)Me (**7a**) (Figure 5). This free (relaxed) ligand **7a** is stabilized by hydrogen bonding N2−H27···O1 (N2−H27 1.022 Å, O1···H27 1.884, N2···O1 2.760 Å, N2−H27−O1 141.8°); this is not the case in platinum complex **6**. Rotation of the −N(R)Me groups (R = H, C(O)Me) around the C−N bonds results in another equilibrium structure **7b** that is no longer stabilized by a hydrogen bond (Figure 5). The ZPE-corrected energy of this conformer (**7b**) is 6.9 kcal/mol higher than that of **7a**. For comparison the calculated structure of the parent diazadiene (MeN=CHCH=NMe, **8**) is also shown in Figure 5. Selected structural parameters of all calculated molecules are given in Table 5.

The conformation of the free ligand **7b** is close to that of the coordinated one in complex **6**. In complex **6** the halves of the ligand (C2,N1,C3,O1 and C2,C1,N2) include an angle of 73.5° (cf. with the corresponding angle of 80(1)° in the experimental complex **4b**). In the free ligand **7b** this interplanar angle amounts to 69.8°, but it is strongly reduced (40.2°) in **7a** as a consequence of the formation of the hydrogen bridge N2−H27···O1. The C1−C2 distance in **7a**/**7b** (1.350/1.347 Å) and bond order (1.741/1.765) show that this bond is a double bond. On the other hand, the C−N bonds have only small (C1−N2 1.378/1.375 Å; BO 1.156/1.160) and no double-bond character (C2−N1 1.427/1.432; BO 0.984/0.957), respectively, as compared with the parent diazadiene **8** (C−C 1.484 Å, BO 1.056; C=N 1.272 Å, BO 1.871) and with the N−CH_3 distances in **7a**/**7b** and **8** (1.448−1.462 Å, BO 0.956−1.031) reveals. Coordination of ligand **7b** to platinum, yielding complex **6**, results in strong elongation of the C1−C2 bond (1.347 vs 1.428 Å, BO 1.765 vs 1.291) that is accompanied by strengthening of the C−N bonds (C1−N2 1.375 vs 1.361 Å, BO 1.160 vs 1.234; C2−N1 1.432 vs 1.457 Å, BO 0.957 vs 0.938). Furthermore, coordination of Pt to O1 results in weakening of the C3=O1 bond (**7b** vs **6**: 1.224 vs 1.249 Å, BO 1.682 vs 1.527).

The path of formation of complexes **4** has not been investigated yet. Intermediates might be acyl(hydrido)platinum(IV) complexes [Pt$(COMe)_2$Cl(H)(RN=CHCH=NR)] (**9**), analogous to complexes **3** when 2,3-dimethyl-substituted diazadiene ligands were used (vide supra). Thus, the molecular structure of [Pt$(COMe)_2$Cl(H)(MeN=CHCH=NMe)] (**9a**) was calculated (Figure 6) on the same level of theory as complex **6**. The calculated structure of complex **9a** is in good agreement with that of analogous complexes with bipyridine coligands [Pt$(COMe)_2$Cl(H)L_2] (L_2 = 4,4′-*tert*-Bu_2bpy (**10a**), 4,4′-*tert*-Bu_2-6-*n*-Bubpy (**10b**)),[5] as shown by the comparison of **9a** with **10a**/**10b**: Pt−Cl 2.512 vs 2.476(2)/2.479(3) Å, Pt−C3 2.059 vs 2.00(1)/2.00(1) Å, Pt−C13 2.033 vs 1.99(1)/2.00(1) Å, C=O 1.212 vs 1.20(1)−1.21(1) Å. The calculated Pt−H bond in **9a** (1.565 Å) is substantially shorter than that in **10a**/**10b** (1.72(5)/1.79(2) Å). Evaluation of ZPE-corrected energies makes it clear that complex **9a** is less stable by 18.2 kcal/mol than complex **6** and that the isomerization **9a** → **6** is a thermodynamically allowed reaction. Thus, these results indicate that reactions of platina-β-diketone **1a** with diazadienes unsubstituted at the 2- and 3-positions may proceed via a platinum(IV) complex of type **9** as an intermediate, yielding complexes **4**, although a direct protonation of the imine cannot be strictly ruled out.

Formation of complex **6** (model for complexes **4**) with its enamine−amide type ligand **7** from acyl(hydrido)platinum(IV) complex **9** remains speculative. A reductive elimination of acetyl and dab ligands with C−N bond formation and hydride transfer from platinum to ligand might be involved. Formally, formation of enamine−amide type ligands in complexes **4** is a 1,4-addition of MeC(O)−H (a tautomer of hydroxycarbene Me−C−OH that is a building block of platina-β-diketones) to the dab ligand. Thus, a new metal-assisted addition reaction to diazadienes may be involved. Other examples for reactions of this type are 1,3-dipolar cycloadditions to M−N=C fragments of diazadiene complexes,[12]

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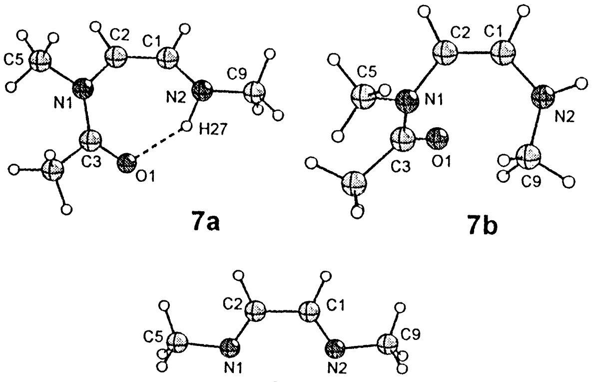
[12] Feiken, N.; Schreuder, P.; Siebenlist, R.; Frühauf, H.-W.; Vrieze, K.; Kooijman, H.; Veldman, N.; Spek, A. L.; Fraanje, J.; Goubitz, K. *Organometallics* **1996**, *15*, 2148 and literature cited therein.

Table 5. Calculated Structural Parameters (Bond Lengths in Å and Angles in deg) for [Pt(COMe)Cl{MeN(H)CH=CHN(Me)C(O)Me}] (6), for the Ligand MeN(H)CH=CHN(Me)C(O)Me with (7a) and without (7b) N−H···O Hydrogen Bonding, and for the Diazadiene MeN=CHCH=NMe (8)[a]

	4d	**6**/BO[b]	**7a**/BO[b]	**7b**/BO[b]	**8**/BO[b]
Pt−C1	2.326(8)	2.304/0.334			
Pt−C2	2.057(9)	2.111/0.410			
Pt−C13	1.968(9)	1.994/0.782			
Pt−Cl	2.332(2)	2.360/0.465			
Pt−O1	2.147(6)	2.358/0.116			
C1−C2	1.43(1)	1.428/1.291	1.350/1.741	1.347/1.765	1.484/1.056
C1−N2	1.33(1)	1.361/1.234	1.378/1.156	1.375/1.160	1.272/1.871
C2−N1	1.45(1)	1.457/0.938	1.427/0.984	1.432/0.957	1.272/1.871
C9−N2	1.48(1)	1.462/0.971	1.456/0.993	1.452/0.983	1.448/1.031
C5−N1	1.52(1)	1.461/0.948	1.462/0.956	1.460/0.960	1.448/1.031
C3−N1	1.33(1)	1.359/1.231	1.371/1.180	1.385/1.135	
C3−O1	1.26(1)	1.249/1.527	1.235/1.597	1.224/1.682	
C13−O2	1.22(1)	1.217/1.777			
C2−Pt−O1	76.7(3)	74.4			
C2−Pt−Cl	168.3(2)	169.2			
O1−Pt−C13	169.2(3)	167.1			
C2−C1−N2	126.5(7)	125.6	129.2	132.3	
C1−C2−N1	118.2(7)	119.5	129.1	128.0	123.5
N1−C3−O1	119.9(8)	120.6	122.2	122.0	123.5
Pt−O1−C3	113.8(6)	110.6			
N1−C2−C1−N2	6(1)	3.8	0.3	2.7	0.1
H2−C2−C1−H1		−21.5	−1.6	0.5	0.1

[a] Experimental values for complex **4d** are given for comparison. [b] Bond order (given in electron pairs).



7a **7b**

8

Figure 5. Calculated structures and numbering schemes of the ligand MeN(H)CH=CHN(Me)C(O)Me with (**7a**) and without (**7b**) NH···O hydrogen bonding and for the diazadiene MeN=CHCH=NMe (**8**).

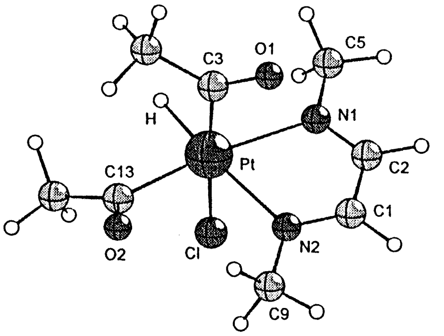


Figure 6. Calculated structure of the acyl(hydrido)platinum(IV) complex $[Pt(COMe)_2Cl(H)(MeN{=}CHCH{=}NMe)]$ (**9a**). Selected bond lengths (in Å) and angles (in deg); bond orders are given in parentheses: Pt−H 1.565 (0.641), Pt−Cl 2.512 (0.255), Pt−C3 2.059 (0.590), Pt−C13 2.033 (0.654), Pt−N1 2.268 (0.169), Pt−N2 2.238 (0.167), C1−C2 1.471 (1.077), C1−N2 1.279 (1.783), C2−N1 1.277 (1.789), C3−O1 1.212 (1.814), C13−O2 1.212 (1.809); H−Pt−N1 99.8, H−Pt−C3 88.5, H−Pt−C13 86.7, H−Pt−Cl 91.2, N1−Pt−N2 74.2, C3−Pt−C13 92.5.

addition of D_2 to coordinated dad ligands, yielding *C*−hydrogenated products,[13] and—even catalytic—1,4-hydrosilylations of diazadienes.[14]

Experimental Section

General Comments. All reactions were performed under an argon atmosphere using standard Schlenk techniques. The solvents were dried and distilled prior to use. NMR spectra were obtained on Varian Gemini 200, VXR 400, and Unity 500 NMR spectrometers using 5 mm tuneable probes. If not indicated otherwise, samples were measured in $CDCl_3$ at 300 K. Chemical shifts are relative to $C\textit{H}Cl_3$ (δ 7.24) and $\textit{C}DCl_3$ (δ 77.0) as internal references. Assignments of NMR signals were partly revealed by $^1H-^1H$ COSY and $^1H-^{13}C$ HETCOR−NMR experiments. The purity of type **2** and **4** complexes was proved by NMR spectroscopic investigations, because satisfactory elemental analysis results could not be obtained with standard procedures. The platina-β-diketone $[Pt_2\{(COMe)_2H\}_2(\mu\text{-}Cl)_2]$ (**1a**) was synthesized according to a published method.[1] Diazadiene ligands were kindly supplied by Prof. J. Scholz (University of Koblenz, Koblenz, Germany) or synthesized according to standard procedures from glyoxal/diacetyl with the requisite amine. Other chemicals were commercial materials used without further purification or after distillation.

$[Pt(COMe)_2\{(n\text{-}Pr)N{=}CMeCMe{=}N(n\text{-}Pr)\}]$ (2a) and [Pt(COMe)Cl(PhN=CMeCMe=NPh)] (2b). At −40 °C, to $[Pt_2\{(COMe)_2H\}_2(\mu\text{-}Cl)_2]$ (**1a**; 100 mg, 0.16 mmol) in thf (5 mL) was added a solution of RN=CMeCMe=NR (R = *n*-Pr, Ph) (0.32 mmol) in thf (5 mL). The reaction mixture was warmed to room temperature over 20 min and then stirred for another 10 min, yielding a clear pale yellow solution. About half (**2a**) and two-thirds (**2b**), respectively, of the solvent were evaporated in vacuo. Addition of diethyl ether (ca. 15 mL) resulted in pale yellow precipitation of the product, which was filtered off, washed with diethyl ether, and dried briefly in vacuo.

Data for complex **2a** are as follows. Yield: 57.5 mg (40%). ^1H NMR ($CDCl_3$, 400 MHz): δ 0.85 (t, 6H, 2 × $C\textit{H}_3$, *n*-Pr),

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[13] Zoet, R.; Elsevier, C. J.; van Koten, G.; Versloot, P.; Vrieze, K.; van Wijnkoop, M.; Duineveld, C. A.; Goubitz, K.; Heijdenrijk, D.; Stam, C. H. *Organometallics* **1989**, *8*, 23.

[14] Brockmann, M.; tom Dieck, H. *J. Organomet. Chem.* **1986**, *314*, 75.

Table 6. Crystal Data and Structure Refinement Details for 2a, 2b·CDCl$_3$, and 4d

	2a	**2b**·CDCl$_3$	**4d**
empirical formula	$C_{14}H_{26}N_2O_2Pt$	$C_{19}H_{19}Cl_4DN_2OPt$	$C_{14}H_{27}ClN_2O_2Pt$
fw	449.46	630.27	485.92
cryst syst	monoclinic	monoclinic	orthorhombic
space group	$P2_1/n$	$P2_1/n$	*Pbca*
a, Å	9.0874(19)	13.903(3)	11.044(2)
b, Å	16.994(7)	8.889(1)	11.875(3)
c, Å	10.755(2)	18.174(5)	26.348(5)
β, deg	99.72(2)	98.38(3)	
V, Å^3	1637.0(8)	2222.1(8)	3455(1)
Z	4	4	8
ρ(calcd), g cm^{-3}	1.824	1.884	1.868
μ(Mo *K*α), mm^{-1}	8.572	6.807	8.279
F(000)	872	1208	1888
scan range, deg	$2.57 < \theta < 26.04$	$2.56 < \theta < 26.06$	$2.41 < \theta < 26.08$
recip lattice segments *h*,*k*,*l*	−10 to +10, −20 to +20, −13 to +13	−17 to +16, −9 to +10, −22 to +22	−13 to +13, −14 to +14, −31 to +32
no. of rflns collected	12 458	12 135	24 187
no. of indep rflns	3035 (R(int) = 0.0623)	4276 (R(int) = 0.0623)	3363 (R(int) = 0.1020)
no. of params refined	276	324	284
goodness of fit on F^2	1.113	1.087	1.109
final R ($I > 2\sigma(I)$)	$R1 = 0.0184$, $wR2 = 0.0430$	$R1 = 0.0315$, $wR2 = 0.0750$	$R1 = 0.0430$, $wR2 = 0.0906$
R, all data	$R1 = 0.0223$, $wR2 = 0.0475$	$R1 = 0.0409$, $wR2 = 0.0827$	$R1 = 0.0667$, $wR2 = 0.1001$
largest diff peak and hole, e Å^{-3}	1.154 and −0.541	1.385 and −1.260	1.521 and −0.914

1.51 (m, 4H, 2 × C*H*$_2$, *n*-Pr), 2.05 (s, 6H, 2 × NCC*H*$_3$), 2.17 (s + d, 6H, $^3J_{\mathrm{Pt,H}} = 19.5$ Hz, 2 × COC*H*$_3$), 3.76 (t, 4H, 2 × C*H*$_2$, *n*-Pr). ^{13}C NMR (CDCl$_3$, 101 MHz): δ 11.2 (s, 2 × *C*H$_3$, *n*-Pr), 17.8 (s, 2 × NC*C*H$_3$), 22.6 (s, 2 × *C*H$_2$, *n*-Pr), 43.6 (s, 2 × CO*C*H$_3$), 56.0 (s, 2 × *C*H$_2$, *n*-Pr), 172.1 (s, 2 × N*C*CH$_3$), 231.6 (s, 2 × *C*OCH$_3$).

Data for complex **2b** are as follows. Yield: 65.2 mg (40%). ^{1}H NMR (CDCl$_3$, 400 MHz): δ 1.62 (s, 3H, NCC*H*$_3$), 1.88 (s, 3H, NCC*H*$_3$), 2.13 (s, 3H, COC*H*$_3$), 7.06 (m, 4H, *H*$_{\mathrm{Ph}}$), 7.29 (m, 2H, *H*$_{\mathrm{Ph}}$), 7.43 (m, 4H, *H*$_{\mathrm{Ph}}$). ^{13}C NMR (CDCl$_3$, 101 MHz): δ 19.7 (s, NC*C*H$_3$), 21.1 (s, NC*C*H$_3$), 39.7 (s + d, $^3J_{\mathrm{Pt,C}} = 101.7$ Hz, CO*C*H$_3$), [121.7, 122.2, 127.5, 128.2, 128.8, 129.6 (s, *C*$_{\mathrm{Ph}}$)], 145.0 (s, *i*-C$_{\mathrm{Ph}}$), 148.2 (s, *i*-C$_{\mathrm{Ph}}$), 172.8 (s, N*C*CH$_3$), 173.5 (s, N*C*CH$_3$), 213.8 (s, *C*OCH$_3$).

[Pt(COMe)Cl{RN(H)CH═CHN(R)C(O)Me}] (4). At −40 °C, to [Pt$_2${(COMe)$_2$H}$_2$(μ-Cl)$_2$] (**1a**; 100 mg, 0.16 mmol) in thf (5 mL) was added RN═CHCH═NR (0.32 mmol) as a solid (R = *c*-Hex, *t*-Bu) or as a solution (R = *n*-Pr, *i*-Pr) in thf (0.5−1 mL). The reaction mixture was warmed to room temperature over 20 min and then stirred for another 10 min, yielding a clear, nearly colorless solution. About half of the solvent was evaporated in vacuo. Addition of diethyl ether (15−20 mL) resulted in a white precipitate of the product that was filtered off, washed with diethyl ether, and dried briefly in vacuo.

Data for complex **4a** (R = *n*-Pr) are as follows. Yield: 65.9 mg (45%). ^{1}H NMR (CDCl$_3$, 400 MHz): δ 0.91 (t, 3H, C*H*$_3$, *n*-Pr), 0.93 (t, 3H, C*H*$_3$, *n*-Pr), 1.54 (m, 1H, CH*H*, *n*-Pr), 1.72 (m, 3H, 3 × CH*H*, *n*-Pr), 2.25 (s, 3H, PtC(O)C*H*$_3$), 2.28 (s, 3H, NC(O)C*H*$_3$), 3.00 (m, 1H, CH*H*, *n*-Pr), 3.24 (m, 1H, CH*H*, *n*-Pr), 3.55 (m, 1H, CH*H*, *n*-Pr), 3.69 (m, 1H, CH*H*, *n*-Pr), 4.92 (s+d, 1H, $^2J_{\mathrm{Pt,H}} = 138.9$ Hz, N−C*H*═), 7.5 (m, 1H, N(H)C*H*═), 8.7 (br, 1H, N*H*). ^{13}C NMR (CDCl$_3$, 125 MHz): δ 11.1 (s, *C*H$_3$, *n*-Pr), 11.2 (s, *C*H$_3$, *n*-Pr), 21.3 (s, 2 × *C*H$_2$, *n*-Pr), 22.2 (s, NC(O)*C*H$_3$), 42.8 (s+d, $^2J_{\mathrm{Pt,C}} = 141.6$ Hz, PtC(O)*C*H$_3$), 52.1 (s, *C*H$_2$, *n*-Pr), 52.2 (s, *C*H$_2$, *n*-Pr), 53.7 (s, N−*C*H═), 157.3 (s, N(H)−*C*H═), 181.2 (s, N*C*(O)CH$_3$), 204.1 (s + d, $^1J_{\mathrm{Pt,C}} = 1121.1$ Hz, Pt*C*(O)CH$_3$).

Data for complex **4b** (R = *i*-Pr) are as follows. Yield: 128.8 mg (88%). ^{1}H NMR (CDCl$_3$, 400 MHz): δ 1.15 (d, 3H, C*H*$_3$, *i*-Pr), 1.21 (d, 3H, C*H*$_3$, *i*-Pr), 1.33 (d, 3H, C*H*$_3$, *i*-Pr), 1.36 (d, 3H, C*H*$_3$, *i*-Pr), 2.26 (s, 3H, NC(O)C*H*$_3$), 2.30 (s, 3H, PtC(O)C*H*$_3$), 3.84 (br, 1H, N−C*H*, *i*-Pr), 4.12 (br, 1H, N(H)−C*H*, *i*-Pr), 4.71 (br, 1H, N−C*H*═), 7.3/7.4 (br/br, 1H/1H, N*H*/N(H)−C*H*═). ^{13}C NMR (CDCl$_3$, 101 MHz): δ 20.1 (s, *C*H$_3$, *i*-Pr), 20.5 (s, *C*H$_3$, *i*-Pr), 20.7 (s, *C*H$_3$, *i*-Pr), 22.2 (s, *C*H$_3$, *i*-Pr), 22.6 (s, NC(O)*C*H$_3$), 42.1 (s + d, $^2J_{\mathrm{Pt,C}} = 147.5$ Hz, PtC(O)*C*H$_3$), 50.2 (s + d, $^1J_{\mathrm{Pt,C}} = 480.5$ Hz, N−*C*H═), 50.4 (s, *C*H, *i*-Pr), 51.4 (s, *C*H, *i*-Pr), 143.6 (s, N(H)−*C*H═), 180.4 (s, N*C*(O)CH$_3$), 202.1 (s + d, $^1J_{\mathrm{Pt,C}} = 1072.4$ Hz, Pt*C*(O)CH$_3$).

Data for complex **4c** (R = *c*-Hex) are as follows. Yield: 144.5 mg (84%). ^{1}H NMR (CDCl$_3$, 500 MHz): δ 1.04−2.12 (m, 20H, C*H*$_2$, *c*-Hex), 2.25 (s, 3H, NC(O)C*H*$_3$), 2.30 (s, 3H, PtC(O)C*H*$_3$), 3.43 (br, 1H, C*H*, *c*-Hex), 3.71 (br, 1H, C*H*, *c*-Hex), 4.76 (br, 1H, N−C*H*═), 7.1/7.4 (br/br, 1H/1H, N(H)−C*H*═/N*H*). ^{13}C NMR (CDCl$_3$, 101 MHz): δ 22.1 (s, NC(O)*C*H$_3$), [24.5, 24.6, 24.9, 25.2, 25.4, 25.5, 30.7, 31.2, 32.9 (s, *C*H$_2$, *c*-Hex)], 42.1 (s + d, $^1J_{\mathrm{Pt,C}} = 152.2$ Hz, PtC(O)*C*H$_3$), 51.7 (s + d, $^3J_{\mathrm{Pt,C}} = 475.8$ Hz, N−*C*H═), 57.5 (s, N*C*H, *c*-Hex), 59.8 (s, N*C*H, *c*-Hex), 143.1 (s, N(H)*C*H═), 180.5 (s, N*C*(O)CH$_3$), 202.0 (s, Pt*C*(O)CH$_3$).

Data for complex **4d** (R = *t*-Bu) are as follows. Yield: 94.9 mg (61%). ^{1}H NMR (CDCl$_3$, 400 MHz): δ 1.43 (s, 9H, C*H*$_3$, *t*-Bu), 1.51 (s, 9H, C*H*$_3$, *t*-Bu), 2.29 (s, 3H, PtC(O)C*H*$_3$), 2.39 (s, 3H, NC(O)C*H*$_3$), 4.3 (d, 1H, N*H*), 5.04 (s + d, 1H, $^2J_{\mathrm{Pt,H}} = 113.1$ Hz, N−C*H*═), 7.0 (m, 1H, N(H)−C*H*═). ^{13}C NMR (CDCl$_3$, 101 MHz): δ 25.1 (s, NC(O)*C*H$_3$), 29.1 (s, *C*H$_3$, *t*-Bu), 30.4 (s, *C*H$_3$, *t*-Bu), 41.5 (s + d, $^2J_{\mathrm{Pt,C}} = 138.4$ Hz, PtC(O)*C*H$_3$), 54.8 (s, *C*, *t*-Bu), 59.0 (s, *C*, *t*-Bu), 59.2 (s + d, $^1J_{\mathrm{Pt,C}} = 393.7$ Hz, N−*C*H═), 127.8 (s, N(H)−*C*H═), 181.7 (s, N*C*(O)CH$_3$), 201.1 (s + d, $^1J_{\mathrm{Pt,C}} = 1075.1$ Hz, Pt*C*(O)CH$_3$).

X-ray Crystallography. Crystals suitable for X-ray diffraction analyses were grown from CDCl$_3$ solution (**2a**, **2b**·CDCl$_3$) or by slow addition of diethyl ether to a dilute thf solution (**4d**). Intensity data were collected on a Stoe IPDS diffractometer with Mo Kα radiation ($\lambda = 0.71073$ Å, graphite monochromator) at 220(2) K. A summary of the crystallographic data, the data collection parameters, and the refinement parameters is given in Table 6. Absorption correction was applied numerically ($T_{\mathrm{min}}/T_{\mathrm{max}}$ 0.14/0.36 (**2a**), 0.34/0.71 (**2b**·CDCl$_3$), 0.35/0.45 (**4d**)). The structures were solved by direct methods with SHELXS-86[15] and refined using full-matrix least-squares routines against F^2 with SHELXL-93.[15] Non-hydrogen atoms were refined with anisotropic displacement parameters. All H atoms except for H1 in complex **4d** were found in the difference Fourier map and refined isotropically. Hydrogen atom H27 of **4d** was refined with the isotropic displacement parameter $U_{\mathrm{eq}} = 0.08$. The hydrogen atom H1 in **4d** was included in a calculated position and refined with an isotropic displacement parameter according to the riding model.

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Computational Details. All DFT calculations were carried out by the Gaussian98[16] program package using the hybrid functional B3LYP.[17] For the main-group atoms the basis set 6-31G*[18] was employed. The valence shell of platinum has been approximated by the split-valence basis set (8s7p6d)/[6s5p3d]; for its core orbitals an effective core potential in combination with consideration of relativistic effects has been used.[19] All systems have been fully optimized without any symmetry restrictions. The resulting geometries were characterized as equilibrium structures by the analysis of the force constants of the normal vibrations. Atomic charges and bond orders were obtained by the natural bond orbital (NBO) analysis of Reed et al.[20] as implemented in Gaussian98.

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Supporting Information Available: Tables giving X-ray crystal structure data for **2a**, **2b**·$CDCl_3$, and **4d**, complete tables of Cartesian coordinates of atom positions calculated for **6**−**8**, and figures giving ^{1}H and ^{13}C NMR spectra of complexes of types **2** and **4**. This material is available free of charge via the Internet at http://pubs.acs.org. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited at the Cambridge Crystallographic Data Centre (CCDC) as Supplementary Publication No. CCDC-185360 (**2a**), No. CCDC-185361 (**2b**·$CDCl_3$), and No. CCDC-185362 (**4d**). 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(0)1223/336-033; e-mail, deposit@ccdc.cam.ac.uk).

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