Notes

Synthesis and Characterization of the First Acyl(hydrido)platinum(IV) Complexes

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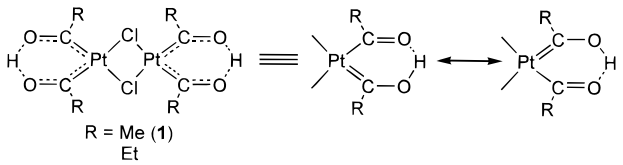
Summary: The platina-β-diketone $[Pt_2\{(COMe)_2H\}_2(\mu\text{-}Cl)_2]$ (**1**) *reacts with 2,2′-bipyridine (bpy), 4,4′-dimethyl-2,2′-bipyridine (me₂bpy), or 4,4′-di(tert-butyl)-2,2′-bipyridine (t-bu₂bpy) to give novel acyl(hydrido)platinum(IV) complexes* $[PtCl(H)(COMe)_2(NN)]$ (*NN = bpy* (**2a**), *me₂bpy* (**2b**), *t-bu₂bpy* (**2c**)). *The complexes* **2** *show an astonishing thermal stability in the solid state up to 180 °C. They decompose with cleavage of acetaldehyde to form the acylplatinum(II) complexes* $[PtCl(COMe)(NN)]$ (**3**). *The identities of* **2** *and* **3** *were determined by microanalysis and NMR (*^1H, ^{13}C*) and IR spectroscopies. The crystal structure of* $[PtCl(H)(COMe)_2(t\text{-}bu_2bpy)]$ (**2c**) *has been determined. The Pt−H bond distance was found to be 1.72(5) Å.*

Introduction

Acyl(hydrido)metal complexes have been proposed as key intermediates in homogeneously catalyzed hydroformylation and aldehyde decarbonylation reactions, as well as in Fischer−Tropsch synthesis. Furthermore, they might be involved as intermediates in the protolysis of metal−acyl bonds and C−H activation reactions of aldehydes.[1] Stable acyl(hydrido)metal complexes with acyl ligands that lack stabilization through chelation are rare and only known with iridium or rhodium as the metal.[2] They are obtained in most cases by oxidative addition of RCHO to low-valent metal complexes. Synthesis of acyl(hydrido)metal complexes starting from the tautomeric hydroxycarbene complexes is not known to date. In an isolated case, Casey et al. described an equilibrium between a hydroxycarbene complex and its isomeric acyl(hydrido)metal complex.[3]

Scheme 1



Recently, we reported the synthesis of the first dinuclear metalla-β-diketones (Scheme 1),[4] which can be regarded as acyl(hydroxycarbene) complexes intramolecularly stabilized by hydrogen bonds.

Compared to the well-known mononuclear carbonyl-substituted metalla-β-diketones of Lukehart[5] that are coordinatively and electronically saturated, complex **1** has a unique reactivity that can be attributed to its electronic unsaturation and its kinetically labile ligand system. The reaction of **1** with aromatic amines leads to complexes of the type $[\{PtCl(RNH_2)(\mu\text{-}COMe)_2Pt[(COR)_2H]\}_2]$ (R = Ph, *p*-Me-C_6H_4) whose crystal structures reveal the formation of Pt_4 zigzag chains.[6] In the course of systematic investigations of the reactivity of these platina-β-diketones, we report here the reaction of **1** with bidentate nitrogen-donor ligands which unexpectedly leads, by oxidative addition, to acyl(hydrido)-platinum(IV) complexes, whose synthesis and reactivity are described.

Results and Discussion

The reaction of $[Pt_2\{(COMe)_2H\}_2(\mu\text{-}Cl)_2]$ (**1**) with 2 equiv of 2,2′-bipyridine (NN = bpy), 4,4′-dimethyl-2,2′-

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(1) (a) Cornils, B.; Herrmann, W. A. *Applied Homogeneous Catalysis with Organometallic Compounds*; VCH: Weinheim, 1996. (b) Parshall, G. W.; Ittel, S. D. *Homogeneous Catalysis*; Wiley: New York, 1992. (c) Milstein, D. *Acc. Chem. Res.* **1988**, *21*, 428. (d) Muetterties, E. L.; Stein, J. *Chem. Rev.* **1979**, *79*, 479. (e) Sola, M.; Ziegler, T. *Organometallics* **1996**, *15*, 2611.

(2) (a) Milstein, D. *Organometallics* **1982**, *1*, 1549. (b) Milstein, D. *J. Am. Chem. Soc.* **1982**, *104*, 5227. (c) Milstein, D.; Fultz, W. C.; Calabrese, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 1336. (d) Bianchini, C.; Meli, A.; Peruzzini, M.; Ramirez, J. A.; Vacca, A.; Vizza, F.; Zanobini, F. *Organometallics* **1989**, *8*, 337. (e) Bianchini, C.; Meli, A.; Peruzzini, M.; Vizza, F.; Bachechi, F. *Organometallics* **1991**, *10*, 820.

(3) In contrast to $[Re\{=C(OH)Me\}(\eta^5\text{-}C_5H_5)(CO)_2]$ (Fischer, E. O.; Riedel, A. *Chem. Ber.* **1968**, *101*, 156), the ring-strain pertubation in $[Re\{=C(OH)(CH_2)_2(\eta^5\text{-}C_5H_4)\}(CO)_2]$ requires an equilibrium with $[Re\{C(O)(CH_2)_2(\eta^5\text{-}C_5H_4)\}(H)(CO)_2]$: (a) Casey, C. P.; Czerwinski, C. J.; Hayashi, R. K. *J. Am. Chem. Soc.* **1995**, *117*, 4189. (b) Casey, C. P.; Czerwinski, C. J.; Fusie, K. A.; Hayashi, R. K. *J. Am. Chem. Soc.* **1997**, *119*, 3971.

(4) (a) Steinborn, D.; Gerisch, M.; Merzweiler, K.; Schenzel, K.; Pelz, K.; Bögel, H.; Magull, J. *Organometallics* **1996**, *15*, 2454. (b) Heinemann, F. W.; Gerisch, M.; Steinborn, D. *Z. Kristallogr.* **1997**, *212*, 181.

(5) Lukehart, C. M. *Adv. Organomet. Chem.* **1986**, *25*, 45.

(6) Steinborn, D.; Gerisch, M.; Heinemann, F. W.; Bruhn, C. *J. Chem. Soc., Chem. Commun.* **1997**, 843.

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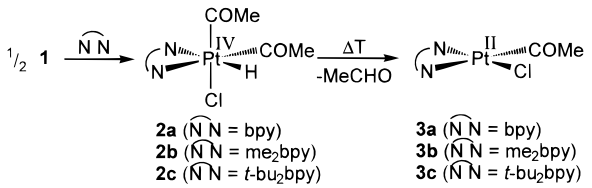
Scheme 2



bipyridine (NN = me_2bpy), and 4,4′-di(*tert*-butyl)-2,2′-bipyridine (*t*-bu_2bpy), respectively, in methylene chloride affords, nearly quantitatively, acyl(hydrido)platinum(IV) complexes [PtCl(H)$(COMe)_2$(NN)] (**2a**−**c**) (Scheme 2).

Intermediates in the formation of **2** might include the cationic Pt^{II} complex [Pt{$(COMe)_2$H}(NN)]Cl, which is converted into **2** as a result of a 1,3-hydrogen shift in the oxidative-addition sense. In the case of treatment of **1** with 1,2-bis(diphenylphosphino)ethane (dppe) at −20 °C, the reaction stops at the level of the cationic complex [Pt{$(COMe)_2$H}(dppe)]Cl.[7] This is further support for the generalization that oxidative additions of Pt^{II} to Pt^{IV} are more facile with nitrogen-supporting ligands than with phosphorus coligands.[8]

The acyl(hydrido)platinum(IV) complexes **2** were obtained as off-white, microcrystalline, moderately air-stable solids. The diastereoisomeric structure shown in Scheme 2 arises from the inequivalence of the two acyl groups and the two halves of the bipyridine ligands as indicated in the ^{1}H and ^{13}C NMR spectra. The large value of the PtH coupling constant for the hydride (**2a**, 1566 Hz; **2b**, 1552 Hz; **2c**, 1541 Hz) is diagnostic of a hydrido ligand *trans* to a nitrogen ligand bound to Pt^{IV}.[9] Furthermore, the similar values of the ^3J(CH) coupling constants (**2a**, 6.8, 5.7 Hz) point to a *cis* orientation of the hydrido ligand with respect to both acyl groups.

Complexes **2** exhibit an astonishing thermal stability (mp (dec) 174 (**2a**), 175 (**2b**), 180 °C (**2c**)). In the solid state, they decompose (180 °C) nearly quantitatively to form [PtCl(COMe)(NN)] (**3**) (Scheme 2) as a result of reductive elimination of acetaldehyde (GC-MS, ^{1}H NMR). In boiling methanol, this reaction is complete within 30 min. Carbonyl complexes are not formed in contrast to the case of the thermal decomposition of [RhCl(H)(COR)$(PMe_3)_3$] (R = Me, Ph, *p*-FC_6H_4, OMe) yielding [RhCl(CO)$(PMe_3)_2$] and RH.[2a]

The high thermal stability of **2** is comparable with the stabilities observed for methyl(hydrido)platinum(IV) complexes of the type [Pt(H)Me_2(NN′N″)] (NN′N″ = a tris(pyrazolyl)borate ligand).[10] However, the thermal stability of **2** is in sharp contrast to the low thermal stability of the corresponding dialkyl(hydrido)platinum(IV) complexes of the type [PtX(H)$(R)_2$(NN)] (X = halide, O_2CCF_3, O_3SCF_3; R = CH_3, CH_2Ph; NN = bidentate nitrogen ligand), which are usually characterized only in situ by ^{1}H NMR spectroscopy at low temperature due to facile decomposition by reductive elimination of RH at room temperature.[9,11]

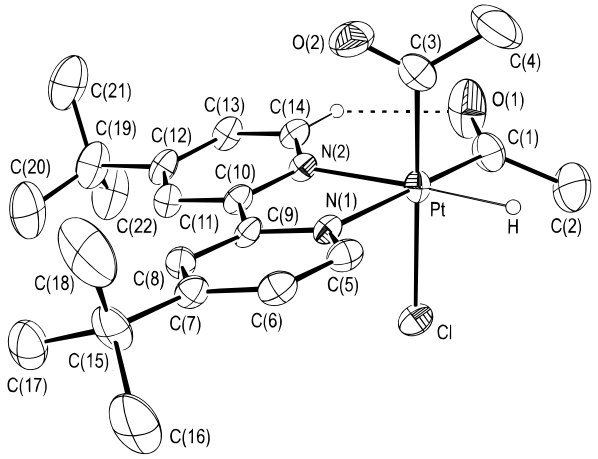


Figure 1. ORTEP-III plot[17] of **2c**, displaying atom-numbering scheme (displacement ellipsoids at 30% probability). Only the H atoms bound to Pt and C14 are shown.

Table 1. Selected Interatomic Distances (Å) and Angles (deg) for [PtCl(H)$(COMe)_2$(*t*-bu_2bpy)] (2c)

Bond Distances			
Pt−N(1)	2.147(6)	Pt−Cl	2.476(2)
Pt−N(2)	2.172(6)	Pt−H	1.72(5)
Pt−C(1)	1.99(1)	C(1)−O(1)	1.20(1)
Pt−C(3)	2.00(1)	C(3)−O(2)	1.20(1)
Bond Angles			
C(3)−Pt−H	91(2)	Cl−Pt−H	90(2)
C(3)−Pt−N(1)	90.2(3)	C(1)−Pt−N(1)	176.3(3)
C(3)−Pt−N(2)	92.0(3)	C(3)−Pt−Cl	179.3(3)
C(1)−Pt−C(3)	92.1(4)	N(2)−Pt−H	177(2)
N(1)−Pt−N(2)	75.9(2)	Pt−C(1)−O(1)	121.5(7)
N(1)−Pt−H	105(2)	Pt−C(1)−C(2)	118.4(7)
C(1)−Pt−H	78(2)	C(2)−C(1)−O(1)	120.1(9)
C(1)−Pt−N(2)	101.1(3)	Pt−C(3)−O(2)	119.8(8)
N(1)−Pt−Cl	89.2(2)	Pt−C(3)−C(4)	120.6(9)
N(2)−Pt−Cl	87.6(2)	C(4)−C(3)−O(2)	120(1)
C(1)−Pt−Cl	88.6(3)		

The molecular structure of **2c** was determined by single-crystal X-ray diffraction (Figure 1). Selected bond lengths and angles are listed in Table 1. The unit cell contains discrete molecules with closest intermolecular contacts between Cl and C6 and C13, respectively (d(C6−Cl) = 3.588 Å, d(C13−Cl) = 3.592 Å). The geometry at the platinum center is close to octahedral. The angles in the plane PtN1N2C1H differ significantly from 90°, due to the restricted bite (∠(N1−Pt−N2) = 75.9(2)°) of the *t*-bu_2bpy ligand.[12] Each ring of the *t*-bu_2bpy ligand is strictly planar (maximal deviation at N1 and N2 of 0.008(5) and 0.021(5) Å, respectively), but they are tilted from each other by 9.6(3)°. These two ring planes of the *t*-bu_2bpy ligand are tilted from the complex plane PtN1N2C1[13] by 8.4(3)° and 12.1(3)°. The

(7) Steinborn, D.; Gerisch, M.; Heinemann, F. W.; Bruhn, C.; Scholz, J. Manuscript in preparation.

(8) Rendina, L. M.; Puddephatt, R. J. *Chem. Rev.* **1997**, *97*, 1735.

(9) (a) de Felice, V.; de Renzi, A.; Panunzi, A.; Tesauro, D. *J. Organomet. Chem.* **1995**, *488*, C13. (b) Holtcamp, M. W.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **1997**, *119*, 848. (c) Wehman-Ooyevaar, I. C. M.; Grove, D. M.; de Vaal, P.; Dedieu, A.; van Koten, G. *Inorg. Chem.* **1992**, *31*, 5484.

(10) (a) O'Reilly, S. A.; White, P. S.; Templeton, J. L. *J. Am. Chem. Soc.* **1996**, *118*, 5684. (b) Canty, A. J.; Dedieu, A.; Jin, H.; Milet, A.; Richmond, M. K. *Organometallics* **1996**, *15*, 2845. (c) Canty, A. J.; Fritsche, S. D.; Jin, H.; Patel, J.; Skelton, B. W.; White, A. H. *Organometallics* **1997**, *16*, 2175.

(11) (a) Stahl, S. S.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **1995**, *117*, 9371. (b) Stahl, S. S.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **1996**, *118*, 5961. (c) Hill, G. S.; Rendina, L. M.; Puddephatt, R. J. *Organometallics* **1995**, *14*, 4966.

(12) Hill, G. S.; Vittal, J. J.; Puddephatt, R. J. *Organometallics* **1997**, *16*, 1209.

(13) Although the H-ligand was found in the difference Fourier map, the calculation of the complex plane around the Pt atom (PtN1N2C1H) was performed without the H atom due to the relative uncertainty in the location of H atoms in heavy atom structures.

(14) Taylor, R.; Kennard, O. *J. Am. Chem. Soc.* **1982**, *104*, 5063.

twist angle N1−C9−C10−N2 amounts to 4(1)°. The plane of the acyl ligand (PtC1C2O1) and the PtN1N2C1 plane form an angle of 24.9(6)°. The C14···O1 distance (d(C14···O1) = 3.06(1) Å, d(CH···O1) = 2.32 Å, ∠(C14−H−O) = 135.8°) indicates a weak hydrogen bond.[14]

The hydrido ligand in **2c** could be located. The Pt−H bond distance was determind to be 1.72(5) Å. The two Pt−C bonds (d(Pt−C1) = 1.99(1) Å, d(Pt−C3) = 2.00(1) Å) and the two C−O bonds (d(C1−O1) = 1.20(1) Å, d(C3−O2) 1.20(1) Å) are of the same lengths. Their magnitudes are in the range of those found for acyl-platinum complexes.[15]

Complexes **2** described here represent the first acyl(hydrido)platinum(IV) complexes. These investigations show that they can be easily synthesized starting from hydroxycarbene complexes. Further investigations into their mechanisms of formation and decomposition are in progress.

Experimental Section

General Comments. All reactions were performed under an Ar atmosphere using standard Schlenk techniques. Solvents were dried prior to use: Et_2O over Na/benzophenone, CH_2Cl_2 over CaH_2, Me_2CO over B_2O_3 followed by 4 Å molecular sieves, and CH_3OH over 4 Å molecular sieves. ^1H and ^{13}C NMR spectra were recorded on Varian Gemini 200 and Varian VXR 400 NMR spectrometers. Chemical shifts are relative to C*H*DCl_2 (δ 5.32) and *C*D_2Cl_2 (δ 53.8) as internal references and to Na_2PtCl_6 (δ 4521 ppm) as an external reference. IR spectra were recorded on a Galaxy FT-IR spectrometer Mattson 5000 using CsBr pellets. The complex [Pt_2{(COMe)$_2$H}$_2$(μ-Cl)$_2$] (**1**) was prepared according to the literature method.[4a]

Preparation of Complexes. [PtCl(H)(COMe)$_2$(NN)] (2). To a suspension of [Pt_2{(COMe)$_2$H}$_2$(μ-Cl)$_2$] (**1**) (200 mg, 0.32 mmol) in methylene chloride (5 mL) at −50 °C was added 2,2′-bipyridine (bpy; 102 mg, 0.66 mmol), 4,4′-dimethyl-2,2′-bipyridine (me$_2$bpy; 120 mg, 0.66 mmol), or 4,4′-di(*tert*-butyl)-2,2′-bipyridine (*t*-bu$_2$bpy; 177 mg, 0.66 mmol). The pale yellow suspension immediately changed color to orange-red. After the solution was warmed to 0 °C over 30 min, the solvent was removed in vacuo to give a pale yellow powder. The residue was dissolved in methylene chloride (10 mL). The solution was filtered, and diethyl ether (15 mL) was added. After standing overnight, the off-white, microcrystalline product was filtered off and dried briefly in vacuo. **2a** (NN = bpy): yield 268 mg, 90%. Mp (dec): 174 °C. Anal. Calcd for $C_{14}H_{15}ClN_2O_2Pt$ (473.81): C, 35.49; H, 3.19; Cl, 7.48; N, 5.91. Found: C, 35.94; H, 3.38; Cl, 7.49; N, 5.98. IR (CsBr): ν(PtH) 2249, ν(CO) 1692, 1666, ν(PtN) 504, ν(PtCl) 250, 240 cm^{-1}. ^1H NMR (200 MHz, CD_2Cl_2): δ −18.32 (s + d, 1H, ^1J(PtH) = 1566 Hz, Pt*H*), 2.28 (s + d, 3H, ^3J(PtH) = 28.0 Hz, CH_3), 2.89 (s + d, 3H, ^3J(PtH) = 30.4 Hz, CH_3) [7.60 (t, 1H), 7.72 (t, 1H), 8.10 (dt, 2H), 8.23 (dd, 2H), 9.05 (d, 1H), 9.55 (d, 1H)]. ^{13}C NMR (101 MHz, CD_2Cl_2): δ 43.4 (s + d, ^2J(PtC) = 289 Hz, *C*H$_3$), 47.0 (s + d, ^2J(PtC) = 227 Hz, *C*H$_3$) [123.4, 2 × 126.4, 126.8, 139.3, 139.4, 149.9, 152.1 (s + d, ^2J(PtC) = 34 Hz), 154.0, 154.2], 191.3 (s + d, ^1J(PtC) = 885 Hz, *C*O), 197.4 (s + d, ^1J(PtC) = 848 Hz, *C*O). ^{195}Pt NMR (86 MHz, CD_2Cl_2): δ 2963 (d, ^1J(PtH) = 1545 Hz). **2b** (NN = me$_2$bpy): yield 300 mg, 95%. Mp (dec): 175 °C. Anal. Calcd for $C_{16}H_{19}ClN_2O_2Pt$ (501.86): C, 38.29; H, 3.82; Cl, 7.06; N, 5.58. Found: C, 37.94; H, 3.66; Cl, 7.28; N, 5.57. IR (CsBr): ν(PtH) 2215, ν(CO) 1698, 1659, ν(PtCl) 241 cm^{-1}. ^1H NMR (200 MHz, CD_2Cl_2): δ −17.83 (s + d, 1H, ^1J(PtH) = 1552 Hz, Pt*H*), 2.31 (s + d, 3H, ^3J(PtH) = 29.0 Hz, COCH_3), 2.49 (s, 3H, CCH_3), 2.60 (s, 3H, CCH_3), 2.96 (s + d, 3H, ^3J(PtH) = 29.3 Hz, COCH_3) [7.45 (m, 2H), 7.93 (s, 1H), 8.69 (d, 1H), 8.84 (d, 1H), 9.31 (d, 1H)]. ^{13}C NMR (101 MHz, CD_2Cl_2): δ 21.4 (C*C*H$_3$), 21.5 (C*C*H$_3$), 43.6 (s + d, ^2J(PtC) = 287 Hz, CO*C*H$_3$), 47.3 (s + d, ^2J(PtC) = 230 Hz, CO*C*H$_3$) [124.4, 2 × 127.3, 128.1, 148.9, 151.6 (s + d, ^2J(PtC) = 34 Hz), 152.2, 152.3, 153.9, 154.1], 191.6 (s + d, ^1J(PtC) = 888 Hz, *C*O), 198.3 (s + d, ^1J(PtC) = 856 Hz, *C*O). **2c** (NN = *t*-bu$_2$bpy): yield 319 mg, 85%. Mp (dec): 180 °C. Anal. Calcd for $C_{22}H_{31}ClN_2O_2Pt$ (586.03): C, 45.09; H, 5.33; Cl, 6.05; N, 4.78. Found: C, 45.05; H, 5.31; Cl, 6.24; N, 4.71. IR (CsBr): ν(PtH) 2233, ν(CO) 1694, 1660, ν(PtCl) 246 cm^{-1}. ^1H NMR (200 MHz, CD_2Cl_2): δ −18.07 (s + d, 1H, ^1J(PtH) = 1541 Hz, Pt*H*), 1.40 (s, 9H, C(CH_3)$_3$), 1.41 (s, 9H, C(CH_3)$_3$), 2.29 (s + d, 3H, ^3J(PtH) = 28.4 Hz, COCH_3), 2.94 (s + d, 3H, ^3J(PtH) = 28.4 Hz, COCH_3) [7.49 (dd, 1H), 7.63 (m, 1H), 8.07 (d, 2H), 8.88 (m, 1H), 9.38 (m, 1H)]. ^{13}C NMR (101 MHz, CD_2Cl_2): δ 31.3 (2 × C(*C*H$_3$)$_3$), 36.4 (*C*(CH$_3$)$_3$), 36.5 (*C*(CH$_3$)$_3$), 44.5 (s + d, ^2J(PtC) = 286 Hz, CO*C*H$_3$), 47.9 (s + d, ^2J(PtC) = 218 Hz, CO*C*H$_3$) [120.8, 120.9, 124.9, 125.4 (s + d, ^2J(PtC) = 18 Hz), 150.8, 153.8 (s + d, ^2J(PtC) = 33 Hz), 155.0, 155.6, 165.0, 165.1], 193.1 (s + d, ^1J(PtC) = 897 Hz, *C*O), 199.6 (s + d, ^1J(PtC) = 856 Hz, *C*O). Resonances of the aromatic H and C atoms of the bipyridine ligands are given in square brackets.

[PtCl(COMe)(NN)] (3). Method A. A solution of [PtCl(H)(COMe)$_2$(bpy)] (**2a**; 100 mg, 0.21 mmol), [PtCl(H)(COMe)$_2$(me$_2$bpy)] (**2b**; 100 mg, 0.20 mmol), or [PtCl(H)(COMe)$_2$(*t*-bu$_2$bpy)] (**2c**; 100 mg, 0.17 mmol) was heated in methanol (10 mL) for 30 min (65 °C). After that, the solution was allowed to stand overnight at ambient temperature, during which time a yellow microcrystalline precipitate formed, which was filtered off and dried briefly in vacuo. **Method B.** [PtCl(H)(COMe)$_2$(bpy)] (**2a**; 100 mg, 0.21 mmol), [PtCl(H)(COMe)$_2$(me$_2$bpy)] (**2b**; 100 mg, 0.20 mmol), or [PtCl(H)(COMe)$_2$(*t*-bu$_2$bpy)] (**2c**; 100 mg, 0.17 mmol) was heated for 10 min at 180 °C. The resulting yellow powder was dissolved in methylene chloride (5 mL). The solution was filtered, and diethyl ether (10 mL) was added. After standing overnight a yellow, crystalline precipitate formed, which was filtered off and dried briefly in vacuo. **3a** (NN = bpy): yield 88 mg, 97%. Anal. Calcd for $C_{12}H_{11}ClN_2OPt$ (429.77): C, 33.54; H, 2.58; Cl, 8.25; N, 6.52. Found: C, 33.84; H, 2.72; Cl, 8.28; N, 6.58. IR (CsBr): ν(CO) 1618, ν(PtCl) 331 cm^{-1}. ^1H NMR (200 MHz, CD_2Cl_2): δ 2.51 (s + d, 3H, ^3J(PtH) = 8.8 Hz, CH_3) [7.43 (t, 1H), 7.62 (q, 1H), 8.08 (m, 4H), 9.05 (d + d, 0.8H, ^3J(PtH) = 68 Hz), 9.33 (d, 0.8H) (the reason for this deviation of the integrated area from that anticipated could not be determined)]. ^{13}C NMR (101 MHz, CD_2Cl_2): δ 42.0 (s + d, ^2J(PtC) = 103 Hz, *C*H$_3$) [122.2, 123.4, 126.5, 127.4 (s + d, ^2J(PtC) = 59 Hz), 138.3, 139.6, 148.3, 151.5 (s + d, ^2J(PtC) = 48 Hz), 154.1, 155.7], 220.2 (s + d, ^1J(PtC) = 989 Hz, *C*O). **3b** (NN = me$_2$bpy): yield 90 mg, 98%. Anal. Calcd for $C_{14}H_{15}ClN_2OPt$ (457.82): C, 36.73; H, 3.30; Cl, 7.74; N, 6.12. Found: C, 37.24; H, 3.56; Cl, 7.58; N, 6.08. IR (CsBr): ν(CO) 1619, ν(PtCl) 330 cm^{-1}. ^1H NMR (200 MHz, CD_2Cl_2): δ 2.43 (s, 3H, CH_3), 2.50 (s, 3H, COCH_3), 2.53 (s, 3H, CH_3) [7.18 (m, 1H), 7.37 (m, 1H), 7.84 (d, 2H), 8.82 (d + d, 0.8H, ^3J(PtH) = 64 Hz), 9.09 (m, 0.8H) (the reason for this deviation of the integrated area from that anticipated could not be determined)]. ^{13}C NMR (101 MHz, CD_2Cl_2): δ 21.8 (*C*H$_3$), 21.9 (*C*H$_3$), 42.1 (s + d, ^2J(PtC) = 110 Hz, CO*C*H$_3$) [123.4, 124.5 (s + d, ^2J(PtC) = 40 Hz), 127.7, 128.6 (s + d, ^2J(PtC) = 56 Hz), 147.8, 151.0, 151.2, 152.3, 154.5, 155.9], 219.9 (*C*O). **3c** (NN = *t*-bu$_2$bpy): yield 88 mg, 96%. Anal. Calcd for $C_{20}H_{27}ClN_2OPt$ (541.98): C, 44.32; H, 5.02; Cl, 6.54;

(15) (a) Klinger, R. J.; Huffman, J. C.; Kochi, J. K. *J. Am. Chem. Soc.* **1982**, *104*, 2147. (b) Anderson, K. G.; Cross, R. J.; Manojlovic-Muir, L.; Muir, K. W.; Solomun, T. *J. Organomet. Chem.* **1979**, *170*, 385. (c) Bardi, R.; Piazessi, A. M.; Cavinato, G.; Caroli, P.; Toniolo, L. *J. Organomet. Chem.* **1982**, *224*, 407.

(16) Sheldrick, G. M. *SHELXS-86, SHELXL-93, Programs for Crystal Structure* Determination; University of Göttingen: Göttingen, Germany, 1986, 1993.

(17) Burnett, M. N.; Johnson, C. K. *ORTEP-III: Oak Ridge Thermal Ellipsoid Plot Program for Crystal Structure Illustrations*. Oak Ridge National Laboratory Report No. ORNL-6895; Oak Ridge National Laboratory: Oak Ridge, TN, 1996.

N, 5.17. Found: C, 43.87; H, 5.04; Cl, 6.61; N, 4.96. IR (CsBr): ν(CO) 1623, ν(PtCl) 333 cm^{-1}. ^{1}H NMR (200 MHz, CD_2Cl_2): δ 1.43 (s, 9H, C(CH_3)$_3$), 1.44 (s, 9H, C(CH_3)$_3$), 2.53 (s, 3H, COCH_3) [7.45 (dd, 1H), 7.64 (dd, 1H), 7.91 (d, 1H), 7.94 (d, 1H), 9.00 (d, 1H), 9.26 (d, 1H)]. ^{13}C NMR (101 MHz, CD_2Cl_2): δ 31.0 (C(*C*H$_3$)$_3$), 31.3 (C(*C*H$_3$)$_3$), 36.5 (*C*(CH$_3$)$_3$), 36.6 (*C*(CH$_3$)$_3$), 43.1 (s + d, ^2J(PtC) = 111 Hz, CO*C*H$_3$) [119.0, 120.2, 124.8, 125.8, 149.4, 152.3, 155.5, 156.9, 163.9, 165.3], 221.8 (*C*O).

X-ray Structure Determination of 2c. Intensity data were collected on a Stoe IPDS diffractometer with Mo Kα radiation (0.7173 Å, graphite monochromator). A summary of the crystallographic data, the data collection parameters, and the refinement parameters is given in Table 2. An absorption correction was carried out numerically (T_{min}/T_{max} 0.15/0.24). The structures were solved by direct methods with SHELXS-86[16] and refined using full-matrix least-squares routines against F^2 with SHELXL-93.[16] Non-hydrogen atoms were refined with anisotropic displacement parameters; H atoms were added to the model in their calculated positions and refined isotropically. The hydrido ligand was found in the difference Fourier map and refined isotropically, although certainty in its location may be compromised by residual electron density near the Pt atom.

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Table 2. Crystal Data and Structure Refinement for 2c

empirical formula	$C_{22}H_{31}ClN_2O_2Pt$
fw	586.03
T, K	220(2)
λ, Å	0.710 73
cryst syst	orthorhombic
space group	$P2_1nb$
a, Å	10.937(3)
b, Å	13.523(4)
c, Å	16.267(5)
V, Å^3	2406(1)
Z	4
ρ_{calc}, g/cm^3	1.618
μ(Mo Kα), mm^{-1}	5.961
F(000)	1152
scan range, deg	$2.70 < \theta < 24.99$
no. of reflns collected	14936
no. of indep reflns	4004 ($R_{int} = 0.0809$)
no. of params refined	257
goodness-of-fit on F^2	0.988
final R ($I > 2\sigma(I)$)	$R_1 = 0.0296$, w$R_2 = 0.0672$
R (all data)	$R_1 = 0.0395$, w$R_2 = 0.0709$
absolute structure param	−0.006(11)
largest diff. peak and hole, e Å^{-3}	1.561 and −0.561

Supporting Information Available: Complete tables of atomic coordinates, H-atom parameters, bond distances, bond angles, and anisotropic displacement parameters for **2c** (8 pages). Ordering information is given on any current masthead page.

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