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Neutral Square-Planar Olefin/Alkyl Platinum(II) Complexes Containing a *N,N′*-Imino−Amide Ligand. Experimental and Theoretical Evidence of Relevant *π*-Back-Donation in the Platinum−Olefin Bond

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A new class of platinum(II) compounds of the formula [PtMe(olefin)(*N,N′*-imino−amide chelate)] is described (olefin = ethylene, propylene, styrene, allyl alcohol, methyl vinyl ketone, methyl acrylate; *N,N′*-imino−amide chelate = *N,N′*-(1,2-dimethyl-1,2-ethanediylidene)bis(2,6-diisopropylaniline)). The neutral complexes exhibit square-planar coordination with a cis arrangement of the olefin and the alkyl group. The compounds have been characterized through one- and two-dimensional NMR spectroscopy, which has disclosed that only one isomer is present in solution. This isomer exhibits the alkene and the N(amido) atom in trans positions, while the alkene substituent is oriented toward the Pt−Me vector. The nature and the arrangement of the ligands seem suitable to favor a *π*-back-donation contribution to the Pt−olefin bond to an extent unprecedented for square-planar compounds, as discussed on the basis of NMR parameters and theoretical calculations.

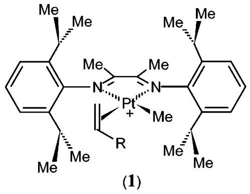
Introduction

Recently,[1] we described a new family of cationic Pt(II) compounds (**1** in Figure 1), showing a cis arrangement of an alkyl group and an olefin.

The compounds are closely related to the catalyst resting states involved in the palladium- and nickel-catalyzed polymerization of alkenes.[2] In these cases, an N,N-chelate with hindrance above and below the coordination plane (i.e. *N,N′*-bis(2,6-diisopropylphenyl)butane-2,3-diimine) is used to favor chain growth by simultaneously inhibiting side reactions. The same steric feature was employed by us to enhance the kinetic inertness of type **1** compounds, thus allowing coordination of a wide variety of alkenes (Figure 1).[1]

In this report, we communicate that a new class of olefin/alkyl complexes can be generated by removing one proton from the ligand backbone of type **1** compounds (Scheme 1).

The corresponding neutral species **2** contain the *N,N′*-imino−amide ligand *N,N′*-(1,2-dimethyl-1,2-ethanediylidene)bis(2,6-diisopropylaniline) (depran), of the general type recently used as an auxiliary in Zr-,[3] Ni-,[4] and Al-catalyzed[5] alkene polymerization.

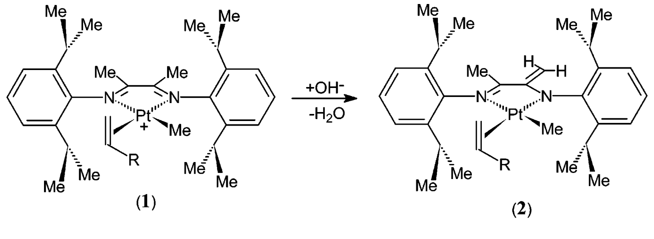


(**1**)

R= H (**a**), Me (**b**), Ph (**c**), CH_2OH (**d**), C(O)Me (**e**), CO_2Me (**f**)

Figure 1. Structure of complexes of type **1**.

Scheme 1. Synthesis of Complexes of Type 2



R= H (**a**), Me (**b**), Ph (**c**), CH_2OH (**d**), C(O)Me (**e**), CO_2Me (**f**)

As described below, the complexes exhibit high selectivity of coordination. Furthermore, the NMR features suggest that an unprecedented degree of *π*-back-donation is involved in the platinum−olefin bond.

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[1] (a) Fusto, M.; Giordano, F.; Orabona, I.; Panunzi, A.; Ruffo, F. *Organometallics* **1997**, *16*, 5981−5987. (b) Ganis, P.; Orabona, I.; Ruffo, F.; Vitagliano, A. *Organometallics* **1998**, *17*, 2646−2650.

[2] Ittel, S. D.; Johnson, L. K.; Brookhart, M. *Chem. Rev.* **2000**, *100*, 1169−1204 and references therein.

10.1021/om049968k CCC: $27.50

Table 1. Selected ^{1}H NMR Data[a] for Type 2 Complexes

compd	formula	Pt−Me[b]	H(olefin)[b]	=CH$_2$
2a	[PtMe(ethylene)(depran)]	−0.26 (77, s, 3H)	2.51 (54, s, 4H)	4.45 (7, s, 1H) 3.88 (s, 1H)
2b	[PtMe(propylene)(depran)]	−0.19 (78, s, 3H)	2.93 (62, m, 1H) 2.65 (65, d, 1H) 2.63 (43, d, 1H)	4.43 (9, s, 1H) 3.81 (s,1H)
2c	[PtMe(styrene)(depran)]	−0.71 (79, s, 3H)	4.45 (74, dd, 1H) 3.05 (42, d, 1H) 2.35 (61, d, 1H)	4.48 (s, 1H) 3.89 (s, 1H)
2d	[PtMe(allyl alcohol)(depran)]	−0.18 (77, s, 3H)	3.09 (58, m, 1H) 2.69 (42, d, 1H) 2.67 (58, d, 1H)	4.51 (9, s, 1H) 3.91 (s, 1H)
2e	[PtMe(methyl vinyl ketone)(depran)]	−0.28 (78, s, 3H)	3.81 (68, dd, 1H) 2.92 (40, d, 1H) 2.27 (56, d, 1H)	4.61 (9, s, 1H) 4.05 (s, 1H)
2f	[PtMe(methyl acrylate)(depran)]	−0.17 (78, s, 3H)	3.32 (65, dd, 1H) 3.07 (38, d, 1H) 2.48 (59, d, 1H)	4.58 (8, s, 1H) 4.02 (s, 1H)

[a] At 298 K and 300 MHz, in CDCl$_3$ (CDCl$_3$, δ 7.26, as internal standard). Abbreviations: s, singlet; d, doublet; dd, double doublet; m, multiplet. [b] ^2J(Pt−H) in parentheses (in Hz; when measurable).

Table 2. Selected ^{13}C NMR Data[a] for Type 2 Complexes

compd	formula	Pt−Me[b]	CH$_2$(olefin)[b] [$\Delta\delta$][d]	CH(olefin)[b] [$\Delta\delta$][e]	=CH$_2$[c]
	ethylene		122.8		
	propylene		115.9	136.2	
	styrene		113.7	136.9	
	allyl alcohol		114.9	137.5	
	methyl vinyl ketone		128.7	137.2	
	methyl acrylate		130.4	128.2	
2a	[PtMe(ethylene)(depran)]	−8.0 (736)	55.6 (196) [67.2]		92.4 (42)
2b	[PtMe(propylene)(depran)]	−6.4 (780)	56.5 (173) [59.4]	72.6 (206) [63.6]	92.1 (45)
2c	[PtMe(styrene)(depran)]	−3.1(777)	48.6 (200) [65.1]	71.8 (198) [65.1]	92.7 (47)
2d	[PtMe(allyl alcohol)(depran)]	−8.0 (750)	55.1 (176) [59.8]	75.0 (224) [62.5]	93.8 (43)
2e	[PtMe(methyl vinyl ketone)(depran)]	−3.0 (731)	48.3 (188) [80.4]	66.3 (192) [70.9]	95.5 (49)
2f	[PtMe(methyl acrylate)(depran)]	−4.2 (738)	50.1 (189) [80.3]	57.3 (214) [70.9]	95.2(42)

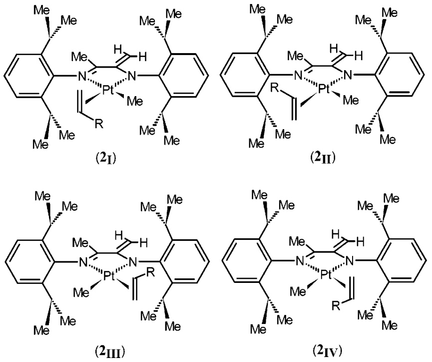
[a] At 298 K and 75.45 MHz, in CDCl$_3$ (^{13}CDCl$_3$, δ 77.0, as internal standard). [b] ^1J(Pt−C) in parentheses (in Hz). [c] ^3J(Pt−C) in parentheses (in Hz). [d] Difference between δ(CH$_2$) of the free olefin and δ(CH$_2$) of the coordinated olefin. [e] Difference between δ(CH) of the free olefin and δ(CH) of the coordinated olefin.

Theoretical considerations are also provided, which give a rationale of this spectral evidence.

Results and Discussion

Synthesis and Characterization of Type 2 Compounds. An immediate reaction takes place when compounds of type **1** are treated with KOH (Scheme 1). The products **2**, isolated in high yields, have been characterized by standard 1D and 2D multinuclear NMR spectroscopy (Tables 1 and 2).

The key points that differentiate the proton NMR spectra of type **2** compounds with respect to type **1** are (i) the resonances of one iminic CH$_3$ group are missing and (ii) two doublets are present in the alkene region that show scalar correlation with the same carbon resonances (ca. 95 ppm) and long-range correlation with the two carbon resonances at higher frequencies. These observations are consistent with the transformation of the [N=CCH$_3$] moiety into [NC=CH$_2$]$^-$ as a consequence of proton abstraction by OH$^-$. Accordingly, a low value of proton−proton scalar coupling constant (ca. 1 Hz) is observed between H$_A$ and H$_B$, as expected for a *gem*-type coupling constant in an sp^2 carbon.[6] In addition, the low-field doublet (H$_B$) shows the typical satellites, due to the scalar coupling with ^{195}Pt ($^4J_{PtH}$ = ca. 5−10 Hz), which also ensures that the ligand is still bonded to platinum.



(2$_{I}$) (2$_{II}$) (2$_{III}$) (2$_{IV}$)

Figure 2. Possible isomers for complexes of type **2** with α-olefins.

With ethylene two isomers can form (**2$_{I}$** and **2$_{III}$**; Figure 2), while with α-olefins up to four species are possible (**2$_{I}$**−**2$_{IV}$**, each one as an enantiomeric couple).

In all cases, a unique spectral pattern has been observed, thus indicating that only one isomer is present

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(3) Kim, Y. H.; Kim, T. H.; Kim, N. Y.; Cho, E. S.; Lee, B Y..; Shin, D. M.; Chung, Y. K. *Organometallics* **2003**, *22*, 1503−1511.

(4) Kim, Y. H.; Kim, T. H.; Lee, B. L.; Woodmansee, D.; Bu, X.; Bazan, G. C. *Organometallics* **2002**, *21*, 3082−3084.

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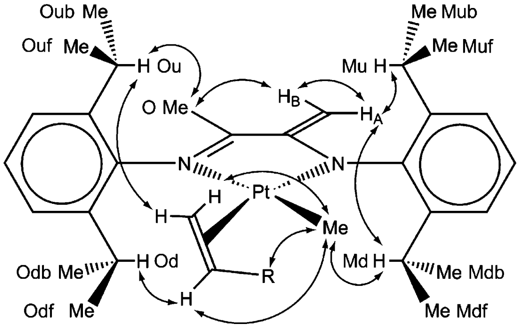

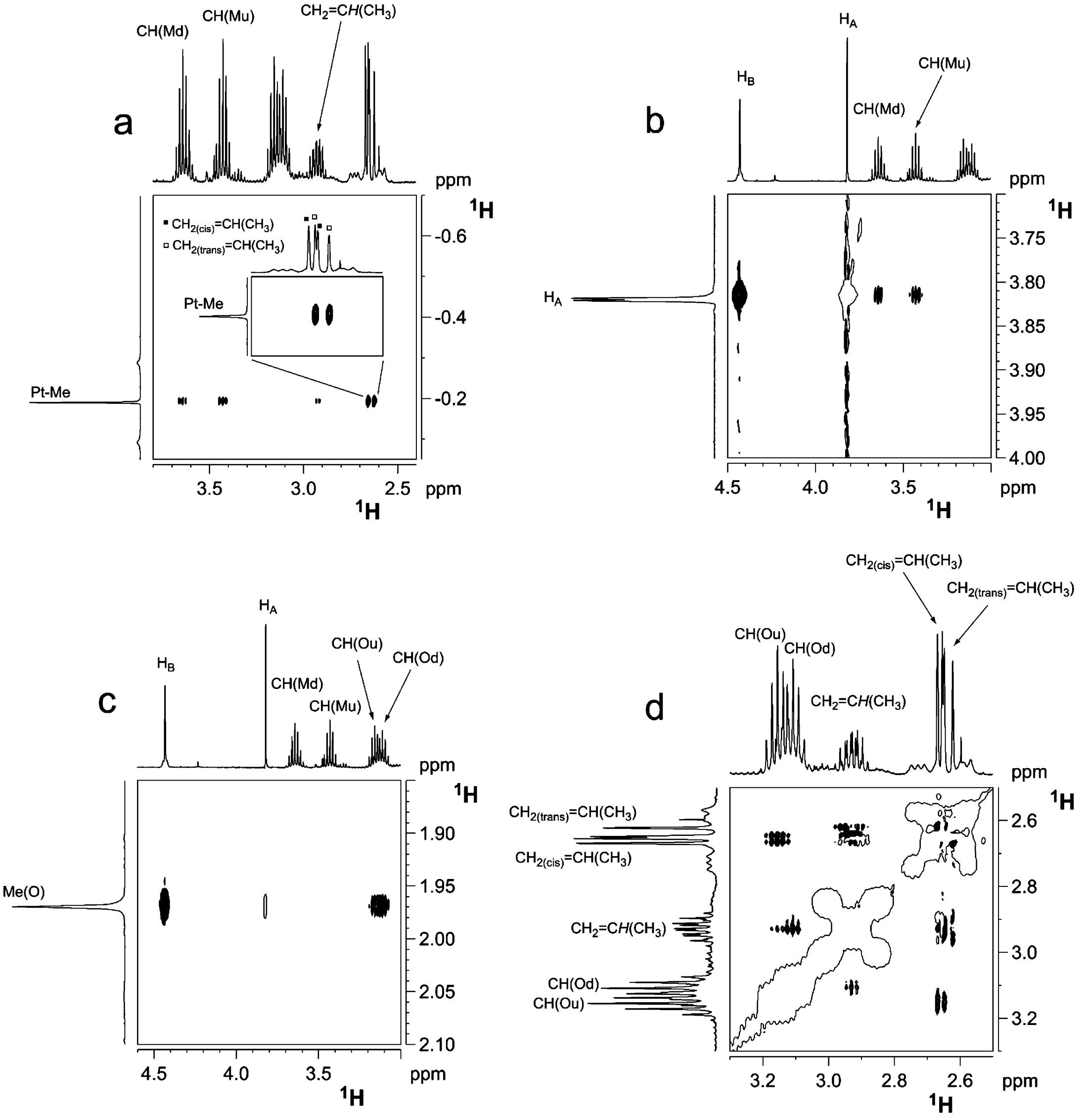

Figure 3. Relevant sections of the ^{1}H-NOESY NMR spectrum of complex **2b**.

in solution. Complete NMR characterization, and in particular NOESY spectroscopy, allows unambiguous determination of the geometrical structure of this isomer.[7] In fact, as observed in previous studies on type **1** and similar compounds,[7] due to the presence of restricted rotations around single bonds (for example, the phenyl rotations around the N−C$_{ipso}$ bond) and to the chirality of the compounds, all the Me resonances show separate signals that can be assigned. In the following, the discussion relative to compound **2b** is given as an example (Figure 3). The low-frequency, easily assignable Pt−Me resonance serves as a starting point. Only two of the four septets due to the isopropyl CH groups give NOESY cross-peaks with Pt−Me, and they are therefore assigned to CH(Mu) and CH(Md)[8] (Figure 3a). The observation of selective strong dipolar

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[7] (a) Macchioni, A.; Magistrato, A.; Orabona, I.; Ruffo, F.; Rothlisberger, U.; Zuccaccia, C. *New J. Chem.* **2003**, 455−458. (b) Zuccaccia, C.; Macchioni, A.; Orabona, I.; Ruffo, F. *Organometallics* **1999**, *18*, 4367−4372.

correlations between CH(Mu) and CH(Md) and one of the two amido–olefinic protons identifies H_A in Figure 3b. The latter interact in a dipolar fashion with H_B, which shows NOE with a methyl group assigned to the backbone Me group (Figure 3c). The resonance of the imino Me group (1.97 ppm) shows strong cross-peaks with the remaining two septets due to the isopropyl CH groups, which are assigned to CH(Ou) and CH(Od).

The further observation that CH(Ou) and CH(Od) interact in a dipolar fashion with the protons of the η^2-coordinated propylene (Figure 3d) finally demonstrates that the isomer present in solution is the one in which the imine arm of the dinitrogen ligand lies in a cis position with respect to the η^2-coordinated propylene ($\mathbf{2_I}$). The spatial orientation of the olefinic moiety deserves additional comment. In particular, as can be seen from Figure 3d, the $CH_2{=}C\mathit{H}(Me)$ proton selectively interacts with CH(Od), while the $C\mathit{H}_{2(cis)}{=}CH(Me)$ proton interacts with CH(Ou), indicating an almost forbidden rotation of the α-olefin around the Pt–alkene bond.[9] The additional observation that the Pt–Me group strongly interacts with $C\mathit{H}_{2(trans)}{=}CH(Me)$ and $CH_2{=}CH(\mathit{Me})$ groups confirms that the η^2-coordinated propylene preferentially orients the Me group toward Pt–Me (isomer $\mathbf{2_I}$).

In all cases the signals of the α-olefin protons show the typical pattern and are significantly shifted to high field with respect to those of the free alkenes of ca. 2–3 ppm. The signals are coupled to ^{195}Pt, which indicates[1a] slow exchange between bound and free alkene at room temperature on the NMR time scale. Rotation of α-olefins along the Pt–alkene bond (i.e., the interconversion $\mathbf{2_I} \rightarrow \mathbf{2_{II}}$) is also inhibited at room temperature, as demonstrated by the presence of selective NOE contacts between the olefin protons and the adjacent ligands, as just mentioned for the propylene compound. Lack of rotation has been attributed to the severe contacts between the olefin substituent and an isopropyl group, which destabilize the $\mathbf{2_{II}}$ isomer.[1a]

On the other hand, ethylene appears as a singlet at 2.51 ppm coupled to ^{195}Pt. The equivalence of the four protons suggests that this unhindered alkene freely rotates at room temperature. At 253 K the singlet is already resolved into two apparent doublets (2.57 and 2.12 ppm, AA′BB′ multiplet), as a consequence of inhibited dynamic behavior. A low-temperature ^{13}C NMR spectrum (233 K in $CDCl_3$) showed substantially no modification of the carbon olefin resonance with respect to those recorded at room temperature ($\Delta\delta = \delta_{298\ K} - \delta_{233\ K} = 0.1$ ppm).

The NMR parameters give useful insight into the nature of the metal–olefin bond in type **2** complexes. It is known that the model originally proposed by Chatt, Dewar, and Duncanson[10] invokes σ-donation from the olefin to the metal and π-back-donation from the metal to the olefin. Several studies have been addressed to appraise the magnitude of these contributions. Most of the studies[11] have been performed on platinum olefin compounds, due to their great chemical inertness and the wide choice of alkenes and coordination environments, although sometimes controversial results were found.[11h,i]

However, it is accepted[12] that in square-planar Pt(II) compounds σ-donation is by far more important than π-back-donation, as demonstrated by the remarkable number of known complexes with electron-rich olefins compared to those containing alkenes with electron-withdrawing substituents.[1b]

Herein, we wish to emphasize that the NMR features give evidence that the coordination environment of type **2** compounds favors π-back-donation to an extent unprecedented for square-planar compounds. The spectral features, which agree with this assertion, are as follows.

(i) Several reports[11a,c,g,i,13] conclude that the high-field coordination shift of the olefin carbons increase with the π-back-donation contribution. As far as we know, the $\Delta\delta$ values found for type **2** compounds are unmatched in Pt(II) square-planar complexes.[14] This is evident by inspection of Table 3, which reports relevant ^{13}C NMR data for a number of representative ethylene and propylene compounds for useful comparison.[23]

It is also interesting to note (see Table 2) that the coordination shift is even more pronounced for the

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[8] "M" and "O" indicate groups that stay in cis positions with respect to methyl and olefin groups, respectively. "u" and "d" discriminate the up and down isopropyl orientations with respect to the olefin R group. Finally, "b" and "f" stand for backward and forward with respect to the plane containing the two phenyl groups (assumed to be coplanar).

[9] Depending on the spectral positions and overlaps of the different resonances, assignment of the "up" and "down" resonances[8] on the ligand arm trans to the olefin was possible by observation of either a weak NOE between the olefin R group and "Md" resonances or a weak NOE between CH(Ou) and CH(Mu) or CH(Od) and CH(Md), respectively.

[10] (a) Dewar, M. J. S. *Bull. Soc. Chim. Fr.* **1951**, *18*, C71–C79. (b) Chatt, J.; Duncanson, L. A. *J. Chem. Soc.* **1953**, 2939–2947.

[11] For relevant studies on platinum(II) complexes, see: (a) Hartley, F. R. In *Comprehensive Organometallic Chemistry*; Pergamon Press: New York, 1982; Vol. 6, p 471. (b) Jesse, A. C.; Stufkens, D. J.; Vrieze, K. *Inorg. Chim. Acta* **1979**, *32*, 87–91. (c) Meester, M. A. M.; Stufkens, D. J.; Vrieze, K. *Inorg. Chim. Acta* **1977**, *21*, 251–258. (d) Cooper, D. J.; Powell, J. *Inorg. Chem.* **1976**, *15*, 1959–1968. (e) Nyburg, S. C.; Simpson, K.; Wong-Ng, W. *J. Chem. Soc., Dalton Trans.* **1976**, 1865–1870. (f) Meester, M. A. M.; van Dam, H.; Stufkens, D. J.; Oskam, A. *Inorg. Chim. Acta* **1976**, *20*, 155–160. (g) Chisholm, M. H.; Clark, H. C.; Manzer, L. E.; Stothers, J. B.; Ward, J. E. H. *J. Am. Chem. Soc.* **1975**, *97*, 721–727. (h) Olah, G. A.; Mo, Y. K. *J. Am. Chem. Soc.* **1972**, *94*, 9244–9246. (i) Chisholm, M. H.; Clark, H. C.; Manzer, L. E.; Stothers, J. B. *J. Chem. Soc.* **1972**, *94*, 5087–5089.

[12] (a) Kurosawa, H.; Ikeda, I. *J. Organomet. Chem.* **1992**, *428*, 289–301. (b) Kurosawa, H.; Urabe, A.; Emoto, M. *J. Chem. Soc., Dalton Trans.* **1986**, 891–893.

[13] See also, for example: (a) Foley, S. R.; Stockland, S. A., Jr.; Shen, H.; Jordan, R. F. *J. Am. Chem. Soc.* **2003**, *125*, 4350–4361. (b) Nicolaides, A.; Smith, J. M.; Kumar, A.; Barnhart, D. M.; Thatcher Borden, W. *Organometallics* **1995**, *14*, 3475–3485. (c) Caruso, F.; Camalli, M.; Pellizer, G.; Asaro, F.; Lenarda, M. *Inorg. Chim. Acta* **1991**, *181*, 167–176. (d) Mink, L.; Rettig, M. F.; Wing, R. M. *J. Am. Chem. Soc.* **1991**, *113*, 2065–2071. (e) Al-Najjar, I. M.; Amin, H. B. *J. Chem. Soc., Dalton Trans.* **1990**, 429–436.

[14] The only exception is given by an elusive hydrido complex (entry 7 of Table 3), characterized at 180 K due to its tendency to undergo insertion of ethylene into the Pt–H bond.

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[22] Shinoda, H.; Yamaguchi, Y.; Saito, Y. *Inorg. Chem.* **1979**, *18*, 673–678.

[23] Higher high-field shifts have been recorded only for three-coordinate Pt(0)[24] or five-coordinate Pt(II)[25] complexes, where the importance of the π-back-donation contribution is acknowledged.

Table 3. ^{13}C NMR Olefin Data[a] for Representative Ethylene and Propylene Compounds of Platinum(II)

entry	formula	CH$_2$(olefin) [$\Delta\delta$][b]	CH(olefin) [$\Delta\delta$][c]	δ(CH) − δ(CH$_2$)	ref
	Ethylene Compounds				
1	[PtMe(ethylene)(depran)] (**2a**)	55.6 (196) [67.2]			
2	[Pt(ethylene){2,6-bis((diphenylphosphino)methyl)pyridine}]$^{2+}$	77.9 (116) [44.9]			15
3	[Pt(ethylene){*cis*-1-(N═CHC$_6$H$_4$)-2-(N═CHPh)C$_6$H$_{10}$}]$^+$	78.0 (153) [44.8]			16
4	[PtMe(ethylene){*N*,*N*′-bis(2,6-diisopropylphenyl)-butane-2,3-diimine}]$^+$ (**1a**)	73.8 (192) [49.0]			1a
5	[PtMe(ethylene){glyoxal bis(2-(methoxymethyl)−4,6-di-*tert*-butylphenyl)imine}]$^+$	74.3 (99)[d] [48.5]			17
6	[Pt$_2$(μ-Cl)$_2$Et$_2$(ethylene)]	63 (260) [59.8]			18
7	[PtH(ethylene){1,2-bis(di-*tert*-butylphosphino)ethane}]$^+$	51.0 (160) [71.8]			19
8	*trans*-[PtCl$_2$(ethylene){*N*-methyl-1-(*N*-methylpyrrol-1-yl)-ethanimine}]	72.2 (168) [50.6]			13e
9	[Pt$_2$(μ-Cl)$_2$Me$_2$(ethylene)$_2$]	63.4 (254) [59.4]			20
10	*trans*-[PtCl$_2$(ethylene)(dimethylamine)]	74.8 (156) [48]			21
11	[PtCl(acetylacetonate)(ethylene)]	67.0 (214) [55.8]			11b
12	*trans*-[PtCl$_2$(ethylene)(4-methyl-pyridine *N*-oxide)]	61.1 (215) [61.7]			11c
13	[PtCl$_3$(ethylene)]$^-$	67.3 (194) [55.5]			11c
14	*trans*-[PtCl$_2$(ethylene)(pyridine)]	75.3 (165) [47.5]			11c
15	*trans*-[PtCl$_2$(ethylene)(4-methylpyridine)]	75.1 (164) [47.7]			11d
	Propylene Compounds				
16	[PtMe(propylene)(depran)] (**2b**)	56.5 (173) [59.4]	72.6 (206) [63.6]	16.1	
17	[Pt(propylene){2,6-bis((diphenylphosphino)methyl)pyridine}]$^{2+}$	74.3 (138) [41.7]	103.5 (108) [31.1]	29.2	15
18	[Pt(propylene){cis−1-(N═CHC$_6$H$_4$)−2-(N═CHPh)C$_6$H$_{10}$}]$^+$	70.8 (155) [45.1]	103.8 (150) [32.4]	33.0	16
19	[PtMe(propylene){*N*,*N*′-bis(2,6-diisopropylphenyl)-butane-2,3-diimine}]$^+$ (**1b**)	70.5 (171) [45.4]	98.0 (185) [38.2]	27.5	1a
20	*trans*-[PtCl$_2$(propylene){*N*-methyl-1-(*N*-methylpyrrol-1-yl)-ethanimine}]	69.8 (160) [46.1]	95.5 (156) [40.7]	25.7	13e
21	*trans*-[PtCl$_2$(propylene)(dimethylamine)]	71.1 (153) [44.8]	98.2 (144) [38.0]	27.1	21
22	*trans*-[PtCl(propylene){*N*-methyl-(*S*)-prolinato}]	71.3 (165) [44.6]	98.2 (154) [38.0]	26.9	22
23	[PtCl(acetylacetonate)(propylene)]	64.9 (210) [51.0]	88.8 (200) [47.4]	23.9	11b
24	*trans*-[PtCl$_2$(propylene)(4-methylpyridine *N*-oxide)]	59.1 (213) [56.8]	83.4 (202) [52.8]	24.3	11c
25	[PtCl$_3$(propylene)]$^-$	66.4 (190) [47.3]	86.9 (188) [49.3]	20.5	11c
26	*trans*-[PtCl$_2$(propylene)(pyridine)]	71.4 (159) [44.5]	99.5 (152) [36.7]	28.1	11c
27	*trans*-[PtCl$_2$(propylene)(4-methylpyridine)]	71.5 (159) [44.4]	99.2 (151) [37.0]	27.7	11d

[a] ^1J(Pt−C) in parentheses (in Hz). [b] Difference between δ(CH$_2$) of the free olefin and δ(CH$_2$) of the coordinated olefin. [c] Difference between δ(CH) of the free olefin and δ(CH) of the coordinated olefin. [d] Average value between those of two diastereomers.

electron-poor olefins, i.e. methyl acrylate and methyl vinyl ketone, where the presence of electron-withdrawing groups is expected to reinforce the charge transfer from the metal.

(ii) A small value for δ(CH) − δ(CH$_2$) of coordinated propylene is also considered diagnostic of high π-back-donation, because “the chemical shifts of saturated sp^3 carbon atoms are less sensitive to methyl substitution of H relative to an olefin sp^2 atom.”[11d] For complex **2b** this difference is only 16.1 ppm, a value which can be usefully compared with the figures reported in Table 3 for representative propylene compounds. In all cases, values higher than 20 have been found, even for [PtCl$_3$(propylene)]$^-$, where the negative charge on the metal is likely to be released through an effective π-back-donation.

(iii) Also, the high-field shift of the olefin protons in the ^{1}H NMR spectra has been used as a probe of the extent of π-back-donation.[26] In this respect, it should be noted that $\Delta\delta$ values for type **2** compounds (2.5−3 ppm) are substantially higher than those typical for Pt(II) square-planar species,[25,27] even by considering that part of the shift is due to the shielding of the aryl rings of depran which face the olefin protons.

(iv) Finally, $^1J_{\mathrm{Pt-C}}$ coupling constants between olefin carbons and ^{195}Pt for type **2** complexes are among the highest of those reported in Table 3 for other square-planar Pt(II) complexes. Also, in this case, a correlation between this spectral evidence and the extent of π-back-donation seems to be valid.[10d,25]

DFT Calculations. A theoretical investigation was undertaken, aiming to verify the actual relationship between the unusual NMR features and the extent of π-back-donation and to rationalize the relevant bonding properties in type **2** compounds. The investigated model systems are reported in Figure 4.

In all of the cases, i.e. with or without a coordinated ethylene molecule, the calculated structures assume a square-planar geometry. The overall structures of the alkene-free species are substantially unmodified by ethylene coordination, with the exception of the Pt−N bond trans to the coordinating olefin. In **1QMa** and **2$_{\mathrm{III}}$QMa** the Pt−N(imino) bond trans to the incoming ethylene molecule is elongated by 0.13 and 0.12 Å relative to **1QM0** and **2$_{\mathrm{III}}$QM0**, respectively. A remarkably different case is **2$_{\mathrm{I}}$QM0**, in which the Pt−N(amido) bond elongates by only 0.05 Å upon olefin coordination. The similar elongation exhibited by the Pt−N(imino) bonds in **1QMa** and **2$_{\mathrm{III}}$QMa** and the remarkably different elongation of the Pt−N(imino) and Pt−N(amido) bonds in **2$_{\mathrm{III}}$QMa** and **2$_{\mathrm{I}}$QMa** clearly indicate that the different behaviors of the Pt−N(imino) and Pt−N(amido) bonds upon ethylene coordination are

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(24) See, for example: van Asselt, R.; Elsevier, C. J.; Smeets, W. J. J.; Spek, A. L. *Inorg. Chem.* **1994**, *33*, 1521−1531.

(25) Albano, V. G.; Natile, G.; Panunzi, A. *Coord. Chem. Rev.* **1994**, *133*, 67−114.

(26) See, for example: Fanizzi, F. P.; Intini, F. P.; Maresca, L.; Natile, G.; Lanfranchi, M.; Tiripicchio, A. *J. Chem. Soc., Dalton Trans.* **1991**, 1007−1015.

(27) (a) van der Poel, H.; van Koten, G. *Inorg. Chem.* **1981**, *20*, 2941−2950. (b) van der Poel, H.; van Koten, G. *Inorg. Chem.* **1981**, *20*, 2950−2956.

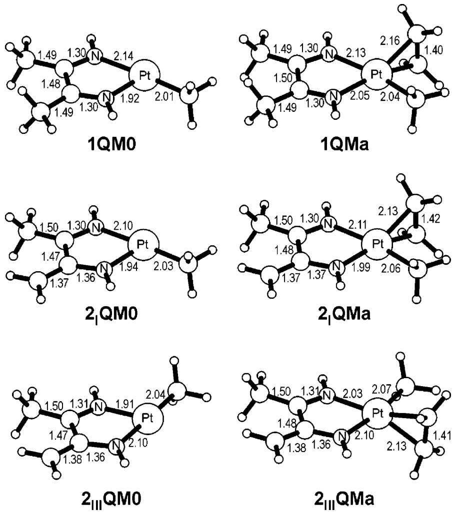


Figure 4. DFT structures of the alkene-free and ethylene-coordinated model systems. **1QMa**, **2_IQMa**, and **2_IIIQMa** are models for the **1a**, **2_Ia**, and **2_IIIa** real systems experimentally investigated. **1QM0**, **2_IQM0**, and **2_IIIQM0** indicate the three alkene-free species obtained by subtracting ethylene from **1QMa**, **2_IQMa**, and **2_IIIQMa**, respectively. Distances are given in Å.

Table 4. Calculated Values for a Series of Common Descriptors (X) Relative to the C=C Bond of Free and Coordinated Ethylene and to the C−C Bond of Ethane[a]

system	bond length (Å)	frequency ($\mathrm{cm^{-1}}$)	^{13}C NMR ($\Delta\delta$)[b]
ethylene	1.33 (2.00)	1637 (2.00)	0 (2.00)
1QMa	1.40 (1.65)	1516 (1.82)	38 (1.68)
2_IQMa	1.42 (1.55)	1492 (1.78)	66 (1.45)
ethane	1.53 (1.00)	974 (1.00)	120 (1.00)

[a] Calculated BO values are given in parentheses, according to the formula BO = 1 + ($X_\mathrm{ethane} - X_\mathrm{complex}$)/($X_\mathrm{ethane} - X_\mathrm{ethylene}$). [b] Calculated $\Delta\delta$ values with respect to free ethylene.

related only to the intrinsic chemical properties of the amido N function. Finally, we unexpectedly calculated the Pt−N(amido) bond in **2_IQM0** to be longer than the corresponding Pt−N(imino) bond in **2_IIIQM0**.

Although the C=C ethylene bond length is rather similar in all the alkene-bound species, it must be noted that it is slightly longer on going from **1QMa** to **2_IIIQMa** and finally to **2_IQMa**. Incidentally, the shorter C=C double bond in **1QMa** corresponds to the longest Pt−C(ethylene) distances. In all the ethylene-coordinated species the olefin is tightly bound to the metal, as indicated by the very high ethylene coordination energies we calculated (47.7, 48.1, and 46.5 kcal/mol for **1QMa**, **2_IQMa**, and **2_IIIQMa**, respectively). With regard to the different stabilities of the **2_IQMa** and **2_IIIQMa** isomers, we calculated **2_IQMa** to be 9.4 kcal/mol more stable than **2_IIIQMa**. Rather similarly, we calculated the alkene-free **2_IQM0** species to be 7.8 kcal/mol more stable than **2_IIIQM0**. The higher stability of the **2_IQM0** and **2_IQMa** isomers, with the Me group trans to the N(imino) atom, is a clear consequence of the strong trans effect of the anionic N(amido) atom.

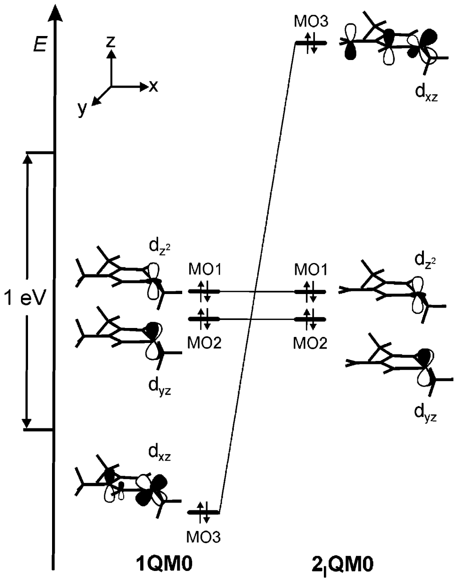


Figure 5. Most of the relevant molecular orbitals of **1QM0** (left) and **2_IQM0** (right). The N−Pt−N bonds lie in the xy plane, and the incoming ethylene molecule approaches the Pt atom along the x axis. For the sake of simplicity the MO1 molecular orbitals of **1QM0** and **2_IQM0** have been sketched as isoenergetic.

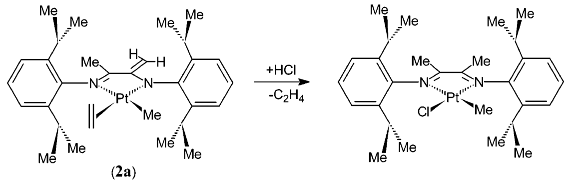
To understand the nature of the Pt−ethylene bond, and its consequences on the ethylene C=C bond, a series of common molecular descriptors were calculated for the C=C bond (Table 4). On the assumption that these descriptors vary linearly with the C=C bond order (BO), we estimated the BO of the C=C double bond of the coordinated ethylene molecule with the formula BO = 1 + ($X_\mathrm{ethane} - X_\mathrm{complex}$)/($X_\mathrm{ethane} - X_\mathrm{ethylene}$), where X is a calculated property between the C=C bond length, the C=C frequency of stretching, and the chemical shift of the C atoms of the C=C bond.

The values in Table 4 indicate that the three estimates of the C=C BO in **2_IQMa** are always smaller than the corresponding ones we calculated for **1QMa**. The smaller difference between the BO of **2_IQMa** and **1QMa** is calculated for the C=C frequency of stretching, with the BO of **1QMa** being only 0.04 greater than the BO of **2_IQMa**, while the greater difference is calculated for the chemical shift of the C atoms, with the BO of **1QMa**, 0.23 being greater than the BO of **2_IQMa**. Incidentally, the coordination shifts calculated for **1QMa** and **2_IQMa** are in excellent agreement with the experimental value (see Table 3). On average, the three general molecular descriptors we used indicate that the BO of **2_IQMa** is 0.13 greater than the BO of **1QMa**, which supports the previously discussed experimental evidence for an enhanced back-donation from the Pt center toward the C=C double bond in **2_IQMa**. Incidentally, the higher back-donation in **2_IQMa** is also supported by the higher coordination energy of ethylene to **2_IQMa**, although ethylene coordination occurs trans to the N(amido) atom: i.e., the N atom with the stronger trans effect.

To understand the origin of this increased back-donation in **2_IQMa**, in Figure 5 we report the most relevant molecular orbitals of **1QM0** and **2_IQM0**.

It is clear that changing the nature of one of the N(imino) atoms of **1QM0** does not change the relative energies of the molecular orbitals MO1 and MO2, with a strong contribution from the metal d_{z^2} and d_{yz} orbitals, respectively, and with MO1 roughly 0.1 eV above MO2 in both **1QM0** and **2_IQM0**. Sharply different is the behavior of MO3, with a strong metal d_{xz} contribution.

Scheme 2. Reaction of 2a with HCl



In **1QM0** this molecular orbital corresponds to HOMO-2 and lies 0.8 eV below HOMO MO1, while in **2_IQM0** MO3 is the HOMO and lies 0.9 eV above MO1. The remarkable increase of energy of the molecular orbital MO3 on going from **1QM0** to **2_IQM0** is a consequence of the interaction between the d_{xz} orbital on the Pt and the p_z orbital on the N(amido) atom. In fact, the p_z orbital on the N(imino) atom in **1QM0** contributes marginally to MO3, whereas in **2_IQM0** there is a strong antibonding interaction between the p_z orbital on the N(amido) atom and the d_{xz} orbital on the metal. This antibonding interaction pushes MO3 up in energy and renders it more prone to back-donate to the π^* orbital of a coordinated alkene. Incidentally, we believe that this antibonding Pt−N(amido) interaction is at the origin of the longer Pt−N(amido) bond in **2_IQM0** relative to the Pt−N(imino) bonds in **1QM0** and **2_{III}QM0** and that its release after ethylene coordination is at the origin of the small elongation of the Pt−N(amido) bond in **2_IQMa** relative to the Pt−N(imino) bonds in **1QMa** and **2_{III}QMa**.

Aiming to compare the calculated bonding properties of type **2** compounds with their actual values, several attempts to grow single crystals for an X-ray diffraction experiment were performed. Unfortunately, in no case were we able to obtain crystals of suitable size.

Reactivity of Type 2 Compounds. Some aspects of the reactivity of the new complexes have been explored. The reaction depicted in Scheme 1 can be reversed. In fact, treating the type **2** complexes with a protic acid containing a poorly coordinating anion readily restores the parent compounds of type **1**. Thus, addition of ethereal HBF_4 to a chloroform solution of **2a** results in immediate and quantitative formation of **1a**, according to the NMR spectrum of the reaction mixture.

Instead, ligand protonation with an acid containing a coordinating anion, i.e. HCl, is accompanied by substitution of the alkene for the chloride, according to Scheme 2.

For all complexes, ^{1}H NMR spectra at 323 K did not show any appreciable variation with respect to those recorded at room temperature, suggesting that dynamic behaviors, concerning olefin exchange or rotation, are not present. The possibility of observing insertion of the alkene into the Pt−Me bond has also been considered. In a previous work,[1b] we described a very rare example of insertion of an olefin into a Pt−alkyl bond, obtained upon heating a chloroform solution of **1f** to 343 K overnight. The same treatment for **2f** was unsuccessful, and the complex was recovered, accompanied by decomposition products. This result is not unexpected, given the higher stability of neutral complexes toward insertion reactions with respect to cationic compounds. At room temperature the decomposition process is obviously slower, and it irreversibly leads to unidentified products within some days.

Conclusion

A new class of neutral olefin/alkyl complexes of platinum(II) of the general formula [PtMe(*N*,*N′*-imino−amido chelate)(olefin)] (**2**) is described. The compounds have been obtained by selective removal of one proton in the presence of a base from the ligand backbone of parent cationic species (**1**) containing an *N*,*N′*-diimino ligand. It should be noted that other examples of the addition of nucleophiles to nickel triad diimine complexes have been reported.[28] However, as far as we know, they promote alternative transformations, e.g. ligand substitution[28a] or addition to the imino double bond.[28b]

A thorough NMR investigation has disclosed high selectivity of coordination for type **2** complexes, as only one isomer has been observed in solution. Its geometry seems dictated by both electronic and steric factors: i.e. the stronger donor ligands Me and N(amido) are in cis positions and the alkene substituent is oriented toward the Pt−Me vector in order to release unfavorable steric congestion.

The olefin coordination shifts lie outside the range commonly observed for square-planar Pt(II) compounds. This unusual evidence has been correlated with a relevant π-back-donation in the Pt−olefin bond, prompted by the nature and the relative arrangement of the ligands. Theoretical calculations strongly support this hypothesis.

Experimental Section

^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on Varian XL-200, Varian Gemini-300, and Bruker Avance DRX-400 spectrometers. ^{1}H-COSY, ^{1}H-NOESY, ^{1}H,^{13}C-HMQC, and ^{1}H,^{13}C-HMBC spectra, using a pulsed field gradient for coherence selection, were recorded on a Bruker Avance DRX-400 spectrometer equipped with a QNP 4-nuclei probe or with a triple-resonance BB inverse probe, both with *z*-gradient coils. $CDCl_3$ was used as solvent; residual $CHCl_3$ (δ 7.26) and $^{13}CDCl_3$ (δ 77.0) were used as internal standards. Complexes of type **1**[1] were obtained according to published methods. ^{1}H−NOESY NMR experiments were recorded using a mixing time of 0.8 s.

Synthesis of Type 2 Complexes. A solution of KOH (0.028 g, 0.50 mmol) in methanol (3 mL) was added to a magnetically stirred suspension of the appropriate precursor (0.50 mmol) in methanol (4 mL) kept in an ice bath. After the mixture was stirred for 15 min, the precipitate was separated, washed with cold methanol, and dried in vacuo. Yield: 70−80%.

[PtMe(ethylene)(depran)] (2a). ^{1}H NMR ($CDCl_3$, 400.13 MHz, 298 K, *J* value in Hz): δ 7.27 (m, aromatic protons cis to olefin), 7.21 (m, aromatic protons cis to Pt−Me), 4.45 (d, $^2J_{HH} = 0.9$, $^4J_{PtH} = 7$, H_B), 3.88 (d, $^2J_{HH} = 0.9$, H_A), 3.48 (sept, $^3J_{HH} = 7.0$, CH(M)), 3.10 (sept, $^3J_{HH} = 7.0$, CH(O)), 2.51 (s, $^2J_{PtH} = 54$, $CH_2{=}CH_2$), 1.99 (s, Me(O)), 1.41 (d, $^3J_{HH} = 7.0$, Me(Ob)), 1.25 (d, $^3J_{HH} = 7.0$, Me(Mf)), 1.21 (d, $^3J_{HH} = 7.0$, Me(Md)), 1.16 (d, $^3J_{HH} = 7.0$, Me(Of)), −0.26 (s, $^2J_{PtH} = 76.7$, Pt−Me). ^{13}C NMR ($CDCl_3$, 100.55 MHz, 298 K, *J* value in Hz): δ 176.5 (s, C=N), 162.7 (s, N*C*=C), 145.3 (s, C_{ipso} cis to Pt−Me), 145.1 (s, quaternary carbons cis to Pt−Me), 139.8 (s, C_{ipso} cis to olefin), 139.6 (s, quaternary carbons cis to olefin), 126.9 (s, *p*-C cis to olefin), 124.9 (s, *p*-C cis to Pt−Me), 123.8 (s, *m*-C cis to olefin), 123.0 (s, *m*-C cis to Pt−Me), 92.4 (s, $^3J_{PtC} = 42$, NC=*C*), 55.6 (s, $^1J_{PtC} = 196$, CH_2CH_2), 27.9 (s, CH(O)), 27.4 (s, CH(M)), 25.2 (s, Me(Mb), 24.6 (s, Me(Of)), 23.9

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(28) (a) Crociani, B.; Antonaroli, S.; Di Bianca, F.; Canovese, L.; Visentin, F.; Uguagliati, P. *J. Chem. Soc., Dalton Trans.* **1994**, 1145−1151. (b) Korybut-Daskiewicz, B. *J. Coord. Chem.* **1992**, 27, 219−221.

(s, Me(Mf)), 23.5 (s, Me(Ob)), 19.8 (s, Me(O)), −8.0 (s, $^{1}J_{PtC}$ = 736.2, Pt−Me). Anal. Calcd for $C_{31}H_{46}N_{2}Pt$: C, 58.02; H, 7.22; N, 4.37. Found: C, 58.29; H, 7.35; N, 4.16.

[PtMe(propylene)(depran)] (2b). ^{1}H NMR (CDCl$_3$, 400.13 MHz, 298 K, *J* value in Hz): δ 7.27 (m, aromatic protons cis to olefin), 7.20 (m, aromatic protons cis to Pt−Me), 4.43 (d, $^{2}J_{HH}$ = 0.9, $^{4}J_{PtH}$ = 9.4, H$_B$), 3.81 (d, $^{2}J_{HH}$ = 0.9, H$_A$), 3.64 (sept, $^{3}J_{HH}$ = 6.9, CH(Md)), 3.42 (sept, $^{3}J_{HH}$ = 6.9, CH(Mu)), 3.15 (sept, $^{3}J_{HH}$ = 6.9, CH(Ou)), 3.11 (sept, $^{3}J_{HH}$ = 6.9, CH(Od)), 2.93 (m, $^{3}J_{HH}$ = 12.7, $^{3}J_{HH}$ = 8.4, $^{3}J_{HH}$ = 6.2, $^{2}J_{PtH}$ = 61.5, CH$_2$═C*H*(CH$_3$)), 2.65 (d, $^{3}J_{HH}$ = 8.4, $^{2}J_{PtH}$ = 65.1, C*H*$_{2(cis)}$═CH(CH$_3$)), 2.63 (d, $^{3}J_{HH}$ = 12.7, $^{2}J_{PtH}$ = 43.0, C*H*$_{2(trans)}$═CH(CH$_3$)), 1.96 (s, Me(O)), 1.41 (d, $^{3}J_{HH}$ = 6.9, Me(Odf)), 1.40 (d, $^{3}J_{HH}$ = 6.9, Me(Ouf)), 1.37 (d, $^{3}J_{HH}$ = 6.2, CH$_2$═CH(C*H*$_3$)), 1.27 (d, $^{3}J_{HH}$ = 6.9, Me(Mfd)), 1.26 (d, $^{3}J_{HH}$ = 6.9, Me(Muf)), 1.21 (d, $^{3}J_{HH}$ = 6.9, Me(Mub)), 1.20 (d, $^{3}J_{HH}$ = 6.9, Me(Mdb)), 1.18 (d, $^{3}J_{HH}$ = 6.9, Me(Odb)), 1.13 (d, $^{3}J_{HH}$ = 6.9, Me(Oub)), −0.19 (s, $^{2}J_{PtH}$ = 78.4, Pt−Me). ^{13}C NMR (CDCl$_3$, 100.55 MHz, 298 K, *J* value in Hz): δ 176.7 (s, C═N), 162.5 (s, N*C*═C), 145.6, 145.3, 145.2 (s, quaternary carbons cis to Pt−Me), 140.0, 139.8, 139.6 (s, quaternary carbons cis to olefin), 127.0 (s, *p*-C cis to olefin), 124.9 (s, *p*-C cis to Pt−Me), 123.9 (s, *m*-C(Ou)), 123.7 (s, *m*-C(Od)), 123.3 (s, *m*-C(Md)), 122.8 (s, *m*-C(Ou)), 92.1 (s, $^{3}J_{PtC}$ = 45, NC═*C*), 72.6 (s, $^{1}J_{PtC}$ = 206.0, CH$_2$═*C*H(CH$_3$)), 56.5 (s, $^{1}J_{PtC}$ = 173.0, *C*H$_2$═CH(CH$_3$)), 27.9 (s, CH(Od)), 27.8 (s, CH(Ou)), 27.4 (s, CH(Md)), 27.3 (s, CH(Mu)), 25.3 (s, Me(Mub) and Me(Mdb)), 24.8 (s, Me(Oub), 24.5 (s, Me(Odb)), 24.0 (s, Me(Muf)), 23.6 (s, Me(Ouf)), 23.4 (s, Me(Odf) and Me(Mdf)), 20.0 (s, Me(O)), 18.0 (s, $^{2}J_{PtC}$ = 17.6, CH$_2$═CH(*C*H$_3$)), −6.4 (s, $^{1}J_{PtC}$ = 780, Pt−Me). Anal. Calcd for $C_{32}H_{48}N_{2}Pt$: C, 58.61; H, 7.38; N, 4.27. Found: C, 58.34; H, 7.20; N, 4.43.

[PtMe(styrene)(depran)] (2c). ^{1}H NMR (CDCl$_3$, 400.13 MHz, 298 K, *J* value in Hz): δ 7.30, 7,10 (m, aromatic protons), 4.48 (d, $^{2}J_{HH}$ = 0.9, H$_B$), 4.45 (dd, $^{3}J_{HH}$ = 13.0, $^{3}J_{HH}$ = 8.7, $^{2}J_{PtH}$ = 74.0, CH$_2$═C*H*Ph), 3.89 (d, $^{2}J_{HH}$ = 0.9, H$_A$), 3.60 (sept, $^{3}J_{HH}$ = 7.0, CH(Md)), 3.37 (sept, $^{3}J_{HH}$ = 7.0, CH(Od)), 3.35 (sept, $^{3}J_{HH}$ = 7.0, CH(Mu)), 3.26 (sept, $^{3}J_{HH}$ = 7.0, CH(Ou)), 3.05 (d, $^{3}J_{HH}$ = 13.0, $^{2}J_{PtH}$ = 41.8, C*H*$_{2(trans)}$═CHPh), 2.35 (d, $^{3}J_{HH}$ = 8.7, $^{2}J_{PtH}$ = 61.0, C*H*$_{2(cis)}$═CHPh), 2.05 (s, Me(O)), 1.50 (d, $^{3}J_{HH}$ = 7.0, Me(Odf)), 1.48 (d, $^{3}J_{HH}$ = 7.0, Me(Ouf)), 1.25 (d, $^{3}J_{HH}$ = 7.0, Me(Odb)), 1.21 (d, $^{3}J_{HH}$ = 7.0, Me(Muf)), 1.20 (d, $^{3}J_{HH}$ = 7.0, Me(Mdb)), 1.19 (d, $^{3}J_{HH}$ = 7.0, Me(Mub)), 1.18 (d, $^{3}J_{HH}$ = 7.0, Me(Oub)), 1.07 (d, $^{3}J_{HH}$ = 7.0, Me(Mdf)), −0.71 (s, $^{2}J_{PtH}$ = 78.6, Pt−Me). ^{13}C NMR (CDCl$_3$, 100.55 MHz, 298 K, *J* value in Hz): δ 176.7 (s, C═N), 162.5 (s, N*C*═C), 145.1, 145.0, 144.8 (s, quaternary carbons cis to Pt−Me), 140.0, 139.9, 139.2 (s, quaternary carbons cis to olefin), 139.6 (s, C$_{ipso}$ olefin),128.4 (s, *o*-C olefin), 127.6 (*m*-C olefin), 127.2 (s, *p*-C cis to olefin), 126.2 (s, *p*-C olefin), 124.9 (s, *p*-C cis to Pt−Me), 124.1 (s, *m*-C(Ou)), 123.8 (s, *m*-C(Od)), 123.0 (s, *m*-C(Md)), 122.9 (s, *m*-C(Ou)), 92.7 (s, $^{3}J_{PtC}$ = 47, NC═*C*), 71.8 (s, $^{1}J_{PtC}$ = 198.0, CH$_2$═*C*HPh), 48.6 (s, $^{1}J_{PtC}$ = 200.0, *C*H$_2$═CHPh), 28.1 (s, CH(Od)), 27.9 (s, CH(Ou)), 27.4 (s, CH(Md)), 27.3 (s, CH(Mu)), 25.6 (s, Me(Mdb)), 25.0 (s, Me(Mub)), 24.9 (s, Me(Odb), 24.7 (s, Me(Oub)), 24.1 (s, Me(Odf)), 23.8 (s, Me(Muf)), 23.6 (s, Me(Ouf)), 23.5 (s, Me(Mdf)), 20.2 (s, Me(O)), −3.0 (s, $^{1}J_{PtC}$ = 776.7, Pt−Me). Anal. Calcd for $C_{37}H_{50}N_{2}Pt$: C, 61.91; H, 7.02; N, 3.90. Found: C, 62.18; H, 7.19; N, 3.77.

[PtMe(allyl alcohol)(depran)] (2d). ^{1}H NMR (CDCl$_3$, 400.13 MHz, 298 K, *J* value in Hz): δ 7.29 (m, aromatic protons cis to olefin), 7.22 (m, aromatic protons cis to Pt−Me), 4.51 (d, $^{2}J_{HH}$ = 1.0, $^{4}J_{PtH}$ = 9.0, H$_B$), 3.91 (d, $^{2}J_{HH}$ = 1.0, H$_A$), 3.62 (sept, $^{3}J_{HH}$ = 6.9, CH(Md)), 3.43 (m, CH$_2$═CHC*H*$_2$OH, spatially close to C*H*$_{2(trans)}$═CHCH$_2$OH) 3.38 (sept, $^{3}J_{HH}$ = 6.9, CH(Mu)), 3.28 (m, CH$_2$═CHC*H*$_2$OH), 3.18 (sept, $^{3}J_{HH}$ = 6.9, CH(Ou)), 3.09 (m, $^{2}J_{PtH}$ = 58.0, CH$_2$═C*H*CH$_2$OH), 3.04 (sept, $^{3}J_{HH}$ = 6.9, CH(Od)), 2.69 (d, $^{3}J_{HH}$ = 13.0, $^{2}J_{PtH}$ = 42.0, C*H*$_{2(trans)}$═CHCH$_2$OH), 2.67 (d, $^{3}J_{HH}$ = 8.3, $^{2}J_{PtH}$ = 58.0, C*H*$_{2(cis)}$═CHCH$_2$OH), 2.01 (s, Me(O)), 1.45 (d, $^{3}J_{HH}$ = 6.9, Me(Odf)), 1.43 (d, $^{3}J_{HH}$ = 6.9, Me(Ouf)), 1.26 (d, $^{3}J_{HH}$ = 6.9, Me(Mdf)), 1.25 (d, $^{3}J_{HH}$ = 6.9, Me(Muf)), 1.21 (d, $^{3}J_{HH}$ = 6.9, Me(Mdb)), 1.20 (d, $^{3}J_{HH}$ = 6.9, Me(Mub)), 1.18 (d, $^{3}J_{HH}$ = 6.9, Me(Odb)), 1.13 (d, $^{3}J_{HH}$ = 6.9, Me(Oub)), −0.18 (s, $^{2}J_{PtH}$ = 77, Pt−Me). ^{13}C NMR (CDCl$_3$, 100.55 MHz, 298 K, *J* value in Hz): δ 177.2 (s, C═N), 162.7 (s, N*C*═C), 145.2 (s, quaternary carbon cis to Pt−Me(down)), 145.10 (s, quaternary carbon cis to Pt−Me(up)),144.6 (s, C$_{ipso}$ cis to Pt−Me), 140.1 (s, quaternary carbon cis to olefin (down)), 139.8 (s, quaternary carbon cis to olefin (up)), 138.9 (s, C$_{ipso}$ cis to olefin), 127.4 (s, *p*-C cis to olefin), 125.3 (*p*-C cis to Pt−Me), 124.1 (s, *m*-C(Od)), 124.0 (s, *m*-C(Ou)), 123.2 (s, *m*-C(Md) and *m*-C(Mu)), 93.8 (s, $^{3}J_{PtC}$ = 43, NC═*C*), 75.0 (s, $^{1}J_{PtC}$ = 194, CH$_2$═*C*HCH$_2$OH), 61.8 (s, CH$_2$═CH*C*H$_2$OH), 55.1 (s, $^{1}J_{PtC}$ = 175, *C*H$_2$═CHCH$_2$OH), 28.0 (s, CH(Od) and CH(Ou)), 27.5 (s, CH(Md) and CH(Mu)), 25.9 (s, Me(Mdb)), 25.6 (s, Me(Mub)), 25.2 (s, Me(Odb)), 25.1 (s, Me(Oub)), 24.4 (s, Me(Mdf)), 24.2 (s, Me(Muf)), 24.1 (s, Me(Odf)), 23.9 (s, Me(Ouf)), 20.1 (s, Me(O)), −8.0 (s, $^{1}J_{PtC}$ = 750, Pt−Me). Anal. Calcd for $C_{32}H_{48}N_{2}OPt$: C, 57.22; H, 7.20; N, 4.17. Found: C, 57.01; H, 7.32; N, 4.36.

[PtMe(methyl vinyl ketone)(depran)] (2e). ^{1}H NMR (CDCl$_3$, 400.13 MHz, 298 K, *J* value in Hz): δ 7.30 (m, aromatic protons cis to olefin), 7.20 (m, aromatic protons cis to Pt−Me), 4.61 (d, $^{2}J_{HH}$ = 0.9, $^{4}J_{PtH}$ = 9.2, H$_B$), 4.05 (d, $^{2}J_{HH}$ = 0.9, H$_A$), 3.81 (dd, $^{3}J_{HH}$ = 12.0, $^{3}J_{HH}$ = 7.9, $^{2}J_{PtH}$ = 68.1, CH$_2$═C*H*COMe), 3.50 (sept, $^{3}J_{HH}$ = 7.0, CH(Md)), 3.31 (sept, $^{3}J_{HH}$ = 7.0, CH(Mu)), 3.21 (sept, $^{3}J_{HH}$ = 7.0, CH(Od)), 3.07 (sept, $^{3}J_{HH}$ = 7.0, CH(Ou)), 2.92 (d, $^{3}J_{HH}$ = 12.0, $^{2}J_{PtH}$ = 39.6, C*H*$_{2(trans)}$═CHCOMe), 2.27 (d, $^{3}J_{HH}$ = 7.9, $^{2}J_{PtH}$ = 55.6, C*H*$_{2(cis)}$═CHCOMe), 2.26 (s, COMe), 2.07 (s, Me(O)), 1.51 (d, $^{3}J_{HH}$ = 7.0, Me(Odf)), 1.41 (d, $^{3}J_{HH}$ = 7.0, Me(Ouf)), 1.22 (m, Me(Muf) and Me(Mdf)), 1.21 (d, $^{3}J_{HH}$ = 7.0, Me(Odb)), 1.19 (d, $^{3}J_{HH}$ = 7.0, Me(Mdb)), 1.18 (d, $^{3}J_{HH}$ = 7.0, Me(Mub)), 1.16 (d, $^{3}J_{HH}$ = 7.0, Me(Oub)), −0.28 (s, $^{2}J_{PtH}$ = 77.5, Pt−Me). ^{13}C NMR (CDCl$_3$, 100.55 MHz, 298 K, *J* value in Hz): δ 200.6 (s, *C*OMe), 176.9 (s, C═N), 162.8 (s, N*C*═C), 144.9 (s, quaternary carbons cis to Pt−Me), 144.2 (s, C$_{ipso}$ cis to Pt−Me), 139.9 (s, quaternary carbon cis to olefin (up)), 139.4 (s, quaternary carbon cis to olefin (down)), 138.6 (s, C$_{ipso}$ cis to olefin), 127.5 (s, *p*-C cis to olefin), 125.6 (*p*-C cis to Pt−Me), 124.4 (s, *m*-C(Ou)), 123.9 (s, *m*-C(Od)), 123.4 (s, *m*-C(Mu)), 123.2 (s, *m*-C(Md)), 95.5 (s, $^{3}J_{PtC}$ = 49.5, NC═*C*), 66.3 (s, $^{1}J_{PtC}$ = 191.8, CH$_2$═*C*HCOMe), 48.3 (s, $^{1}J_{PtC}$ = 187.7, *C*H$_2$═CHCOMe), 29.4 (s, CO*Me*), 28.1 (s, CH(Od)), 27.9 (s, CH(Ou)), 27.5 (s, CH(Md)), 27.4 (s, CH(Mu)), 25.5 (s, Me(Mdb)), 25.0 (s, Me(Mub)), 24.8 (s, Me(Odb), 24.7 (s, Me(Oub)), 23.9 (s, Me(Odf)), 23.8 (s, Me(Muf)), 23.6 (s, Me(Mdf)), 23.5 (s, Me(Ouf)), 20.2 (s, Me(O)), −3.0 (s, $^{1}J_{PtC}$ = 730.6, Pt−Me). Anal. Calcd for $C_{33}H_{48}N_{2}OPt$: C, 57.97; H, 7.08; N, 4.10. Found: C, 57.75; H, 7.00; N, 4.21.

[PtMe(methyl acrylate)(depran)] (2f). ^{1}H NMR (CDCl$_3$, 400.13 MHz, 298 K, *J* value in Hz): δ 7.28 (m, aromatic protons cis to olefin), 7.20 (m, aromatic protons cis to Pt−Me), 4.58 (d, $^{2}J_{HH}$ = 1.1, $^{4}J_{PtH}$ = 8.1, H$_B$), 4.02 (d, $^{2}J_{HH}$ = 1.1, H$_A$), 3.55 (s, COOMe), 3.46 (sept, $^{3}J_{HH}$ = 6.9, CH(Md)), 3.34 (sept, $^{3}J_{HH}$ = 6.9, CH(Mu)), 3.32 (dd, $^{3}J_{HH}$ = 12.1, $^{3}J_{HH}$ = 8.2, $^{2}J_{PtH}$ = 65.0, CH$_2$═C*H*COOMe), 3.21 (sept, $^{3}J_{HH}$ = 6.9, CH(Od)), 3.07 (d, $^{3}J_{HH}$ = 12.1, $^{2}J_{PtH}$ = 38.0, C*H*$_{2(trans)}$═CHCOOMe), 3.03 (sept, $^{3}J_{HH}$ = 6.9, CH(Ou)), 2.48 (d, $^{3}J_{HH}$ = 8.2, $^{2}J_{PtH}$ = 59.0, C*H*$_{2(cis)}$═CHCOOMe), 2.05 (s, Me(O)), 1.49 (d, $^{3}J_{HH}$ = 6.9, Me(Odf)), 1.41 (d, $^{3}J_{HH}$ = 6.9, Me(Ouf)), 1.24 (d, $^{3}J_{HH}$ = 6.9, Me(Muf)), 1.19 (m, Me(Mub) and Me(Mdf)), 1.18 (d, $^{3}J_{HH}$ = 6.9, Me(Mdb)), 1.17 (d, $^{3}J_{HH}$ = 6.9, Me(Odb)), 1.15 (d, $^{3}J_{HH}$ = 6.9, Me(Oub)), −0.17 (s, $^{2}J_{PtH}$ = 78, Pt−Me). ^{13}C NMR (CDCl$_3$, 100.55 MHz, 298 K, *J* value in Hz): δ 176.7 (s, C═N), 169.5 (s, *C*OOMe), 162.9 (s, N*C*═C), 145.1 (s, quaternary carbon cis to Pt−Me(down)), 145.10 (s, quaternary carbon cis to Pt−Me(up)), 144.5 (s, C$_{ipso}$ cis to Pt−Me), 140.1 (s, quaternary carbon cis to olefin (down)), 139.7 (s, quaternary carbon cis to olefin (up)), 138.8 (s, C$_{ipso}$ cis to olefin), 127.4 (s, *p*-C cis to olefin), 125.4 (*p*-C cis to Pt−Me), 124.2 (s, *m*-C(Od)), 124.1 (s, *m*-C(Ou)), 123.3 (s, *m*-C(Md)), 123.1 (s, *m*-C(Mu)), 95.2 (s, $^{3}J_{PtC}$ = 42, NC═*C*), 57.4 (s, $^{1}J_{PtC}$ = 175, CH$_2$═*C*HCOOMe), 51.6 (s, CH$_2$═CHCOO*Me*), 50.1 (s, $^{1}J_{PtC}$ = 168, *C*H$_2$═CHCOOMe), 28.2 (s, CH(Od)), 27.9 (s, CH(Ou)), 27.5 (s, CH(Md)), 27.4 (s, CH(Mu)), 25.3 (s, Me(Odb)), 25.2 (s, Me(Mdf)), 24.9 (s, Me(Mdb)), 24.8 (s, Me(Mub)), 23.9 (s, Me(Muf)), 23.7 (s, Me(Ouf)), 23.5 (s, Me(Oub)), 23.4 (s, Me(Odf)), 20.2 (s, Me(O)), −3.8 (s, $^1J_{\mathrm{PtC}} = 730$, Pt−Me). Anal. Calcd for $C_{33}H_{48}N_2O_2Pt$: C, 56.64; H, 6.91; N, 4.00. Found: C, 56.48; H, 6.77; N, 3.83.

Computational Details. All the structures discussed were calculated with the Amsterdam Density Functional (ADF) program.[29−31] The electronic configurationa of the molecular systems were described by a triple-ζ STO basis set on Pt for 4f, 5s, 5p, 5d, 6s, and 6p (ADF basis set IV).[31] Double-ζ STO basis sets were used for nitrogen and carbon (2s and 2p) and hydrogen (1s), augmented with a single 3d, 3d, and 2p function, respectively (ADF basis set III).[31] The inner shells on platinum (including 4d) and nitrogen and carbon (1s) were treated within the frozen core approximation. Energies and geometries were evaluated by using the local exchange-correlation potential by Vosko et al.,[32] augmented in a self-consistent manner with Becke's[33] exchange gradient correction and Perdew's[34,35] correlation gradient correction. Relativistic effects were included self-consistently with the ZORA formalism.[36,37] The carbon chemical shifts were calculated with the NMR program distributed with the ADF package[31] and developed by Ziegler and co-workers.[38−40]

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