Electrophilic Activation: Unexpected Metal−Metal Bond-Assisted Tl^+ Chelation by a Pt-Benzyl Moiety Instead of Chloride Abstraction

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One of the activation procedures most frequently used in late transition metal chemistry consists in generating cationic metal complexes by halide abstraction from the metal center in the presence of a weakly coordinating anion. We report here on the major effect of replacing Ag(I) with Tl(I) salts, although they are often used indiscriminately as halide abstractors. The Pt(II) complex [Pt(CH_2Ph)Cl(PCH_2-ox)] (**1**) (PCH_2-ox = κ^2-*P*,*N*-(oxazolinylmethyl)-diphenylphosphine) yielded the expected metathesis product [Pt(CH_2Ph)(OTf)(PCH_2-ox)] (**2**) when treated with 1 equiv of AgOTf (OTf = SO_3CF_3) in CH_2Cl_2. In a coordinating solvent such as acetonitrile, chloride displacement readily afforded [Pt(CH_2Ph)($NCCH_3$)(PCH_2-ox)]X (**3**), irrespective of the nature of the halide abstractor ($M^+ = Ag^+$ or Tl^+) and counterion ($X^- = OTf^-$, BF_4^-, PF_6^-) used. Reaction of **1** in CH_2Cl_2 with only half an equivalent of $AgBF_4$ afforded the new, chloride-bridged dinuclear complex [{Pt(CH_2Ph)(PCH_2-ox)}$_2$(μ-Cl)]BF_4 (**5**·BF_4), which results from trapping of the cation [Pt(η^3-CH_2Ph)(PCH_2-ox)]$^+$ (**4**) by unreacted **1**. Similarly, the Pt/Pd heterometallic, single-chloride bridged complex [{Pt(CH_2Ph)(PCH_2-ox)}(μ-Cl){PdMe(PCH_2-ox)}]BF_4 (**6**·BF_4) was obtained by reaction of **4** with [PdClMe(PCH_2-ox)] in a 1:1 ratio. When **1** was reacted in CH_2Cl_2 with Tl^+ instead of Ag^+, formation of **4** was not observed and the main product was an unexpected adduct of Tl^+ to **1** whose X-ray analysis established the formation of both a Pt−Tl bond and a η^6-benzyl−Tl interaction. This bimetallic complex, [(PCH_2-ox)ClPtTl{μ-(η^1-CH_2;η^6-C_6H_5)CH_2Ph}(*Pt*−*Tl*)]PF_6 (**7**·PF_6), is to our knowledge the first metal−metal bonded Tl−Pt−Cl complex to be fully characterized. The coordination geometry around Pt(II) is square-pyramidal, with Tl(I) in the apical position. The Pt−Tl distance of 3.0942(9) Å corresponds to a metal−metal bond that results mainly from donation of electron density from the Pt(II) $5d_{z^2}$ orbital to the vacant Tl(I) $6p_z$ orbital. The Pt−Tl bond is not exactly orthogonal to the Pt(II) square-plane (angle of 70(3)°), but parallel to the C(1)−C(2) bond, thus allowing better π-donation from the benzyl ligand to Tl^+. When the corresponding benzoyl complex [Pt{C(O)Ph}Cl(PCH_2-ox)] (**9**) was reacted with MX ($M^+ = Ag^+$, Tl^+) in CH_2Cl_2, only chloride abstraction and CO deinsertion occurred. Our findings explain why halide abstraction to generate a cationic metal complex with enhanced (catalytic) reactivity may not come to full completion or fail owing to trapping of the cationic complex or "capture" of Tl^+ by the neutral precursor acting, in our case, as an unprecedented chelate through metal−metal bond formation and benzyl coordination. The crystal structures of **1**, **5**·BF_4·0.5CH_2Cl_2, **7**·PF_6, **9**·0.5CH_2Cl_2, and **10**·PF_6·0.75C_4H_8O have been determined by X-ray diffraction.

Introduction

Generating cationic metal complexes represents a general strategy to enhance stoichiometric and catalytic reactivity toward unactivated[1] or electron-rich substrates, which is very often performed in situ.[2] A potentially vacant or lightly stabilized coordination site at the metal center facilitates substrate binding and activation. One of the activation procedures most frequently used in late transition metal chemistry consists in halide abstraction from the metal center in the presence of a weakly coordinating anion (WCA).[3] If the

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‡ X-ray structure analyses, Laboratoire DECMET.

(1) For C−H bond activation in arenes and alkanes see: (a) *Activation and Functionalization of C−H Bonds*; Goldberg, K. I., Goldman, A. S., Eds.; ACS Symposium Series 885; 2004. (b) Jia, C.; Kitamura, T.; Fujiwara, Y. *Acc. Chem. Res.* **2001**, *34*, 633−639. (c) Crabtree, R. H. *Dalton Trans.* **2003**, 3985−3990.

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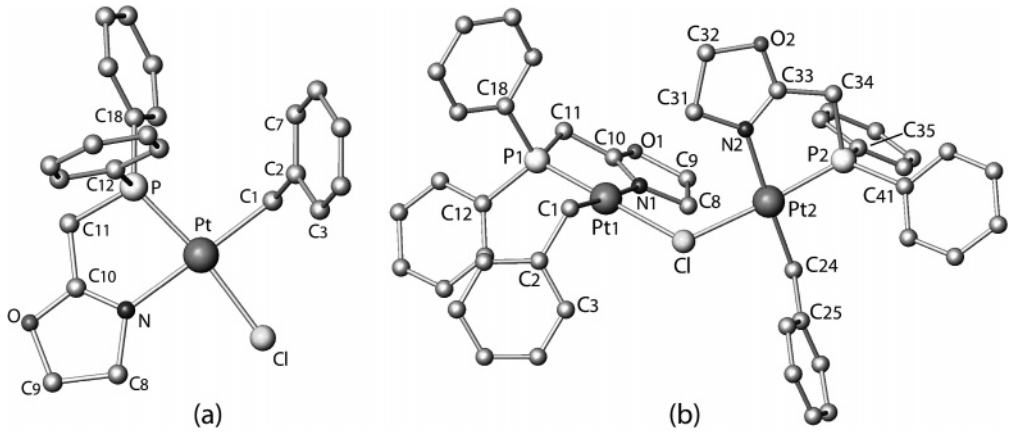


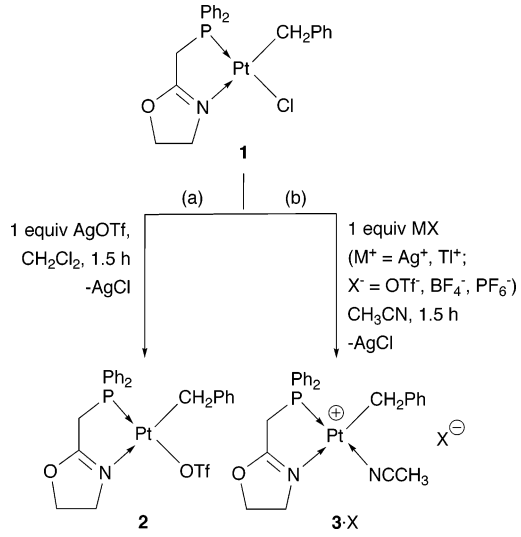
Figure 1. Views of the molecular structures of **1** (a) and **5** (b) in $\mathbf{5}\cdot BF_4\cdot 0.5CH_2Cl_2$. The hydrogen atoms, the counterion, and the solvent have been omitted for clarity. Selected bond distances (Å) and angles (deg) for **1**: Pt−C1 2.055(6), Pt−N 2.120(5), Pt−P 2.192(1), Pt−Cl 2.359(1), C1−C2 1.514(9); C1−Pt−P 98.0(2), N−Pt−P 81.7(1), C1−Pt−Cl 90.2(2), N−Pt−Cl 90.4(1), C2−C1−Pt 115.9(4). Selected bond distances (Å) and angles (deg) for $\mathbf{5}\cdot BF_4\cdot 0.5CH_2Cl_2$: Pt1−C1 2.081(9), Pt1−N1 2.137(7), Pt1−P1 2.179(3), Pt1−Cl 2.401(2), C2−C1 1.53(1), Pt2−C24 2.08(1), Pt2−N2 2.109(8), Pt2−P2 2.177(2), Pt2−Cl 2.390(2), C24−C25 1.51(1); C1−Pt1−P1 94.5(3), N1−Pt1−P1 82.6(2), C1−Pt1−Cl 88.4(3), N1−Pt1−Cl 94.6(2), C2−C1−Pt1 110.9(6), C24−Pt2−P2 93.8(3), N2−Pt2−P2 83.8(2), C24−Pt2−Cl 89.6(3), N2−Pt2−Cl 92.8(2), C25−C24−Pt2 119.2(6), Pt2−Cl−Pt1 119.1(1).

influence of the anion on the nature and catalytic activity of the resulting cationic complex has been clearly evidenced,[3c,4] that of the halide-abstracting Lewis acid (e.g., Ag^+, Tl^+, Na^+, NR_4^+, or $ZnCl_2$) should also be carefully considered because of its possible relevance to the activation procedure, as demonstrated here.

With the hope of isolating and fully characterizing reaction intermediates that would be too reactive with the catalytically most relevant metals, such as Pd(II), we focused on Pt(II) systems and report here on the major effect of replacing Ag(I) with Tl(I) salts, although they are often used indiscriminately as halide abstractors. The Pt(II) complex $[Pt(CH_2Ph)Cl(PCH_2\text{-ox})]$ (**1**) (PCH_2-ox = κ^2-*P*,*N*-(oxazolinylmethyl)diphenylphosphine) (see Figure 1a) was chosen as a model system and is related to Ni(II) and Pd(II) complexes recently used in ethylene oligomerization,[5] CO/olefin copolymerization,[6] or allylic alkylation.[7] Whereas **1** did not react with NH_4PF_6 or $NaBPh_4$ in THF, it quantitatively yielded the expected metathesis product $[Pt(CH_2Ph)(OTf)(PCH_2\text{-ox})]$ (**2**) when treated with 1 equiv of AgOTf (OTf = SO_3CF_3) in CH_2Cl_2. In a coordinating solvent like acetonitrile, chloride displacement readily afforded $[Pt(CH_2Ph)(NCCH_3)(PCH_2\text{-ox})]^+X^-$ (**3**), irrespective of the nature of the halide abstractor ($M^+ = Ag^+$ or Tl^+) and counterion ($X^- = OTf^-$, BF_4^-, PF_6^-) used.

In the absence of relatively good donor ligands, such as OTf^- or acetonitrile, abstraction of the halide from **1** by 1 equiv of $AgBF_4$ or $AgPF_6$ in CH_2Cl_2 resulted in the formation of a dynamic, cationic complex. It was formulated as $[Pt(CH_2Ph)(PCH_2\text{-ox})]^+$ (**4**) on the basis of its ES mass spectrum, which shows only one peak at *m/z* 555 with the correct isotopic distribution. This complex is likely to contain an η^3-benzyl ligand,[8] as supported by its quantitative conversion to **3** upon dissolution in $CDCl_3$ containing a drop of acetonitrile ($^{31}P\{^1H\}$ NMR monitoring).

Scheme 1



Reaction of **1** in CH_2Cl_2 with only half an equivalent of $AgBF_4$ afforded the new, chloride-bridged dinuclear complex **5** (Scheme 2). It clearly results from trapping of the cation **4** by unreacted **1**, and accordingly, **5** was also obtained by reaction of **4** with 1 equiv of **1** in CH_2Cl_2. Such complexes with a single halide bridge[9] are attracting renewed interest because they illustrate a possible deactivation route of cationic catalytic intermediates.[10] Only four dinuclear, single-bridged Pt(II) chloro complexes appear to have been structurally characterized (CSD version 5.25).[11] The Pt1−Cl−Pt2 angle in **5** is 119.1(3)°, and the Pt−Cl distances of

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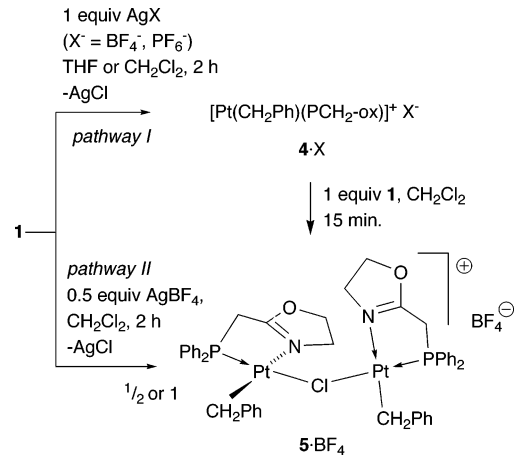
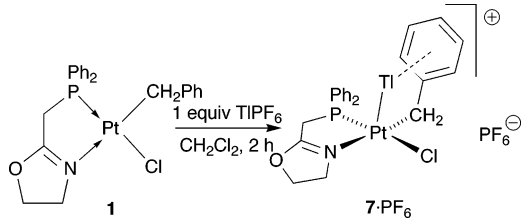
Scheme 2. Synthesis of 4 and 5



Scheme 3



2.401(2) and 2.390(2) Å are, as expected, slightly longer than that in **1** (2.359(1) Å) (Figure 1b). The two metal coordination planes are almost orthogonal to each other (87(1)°).

Reaction pathway I in Scheme 2 suggests a possible extension to the synthesis of heterometallic single-chloride-bridged complexes. Reaction between **4** and [PdClMe(PCH$_2$-ox)][6] in a 1:1 ratio indeed yielded [{Pt(CH$_2$Ph)(PCH$_2$-ox)}(μ-Cl){PdMe(PCH$_2$-ox)}]BF$_4$ (**6**·BF$_4$). Both, the Pt/Pt (**5**·BF$_4$) and Pt/Pd (**6**·BF$_4$) complexes react irreversibly with acetonitrile by splitting of the bridge to afford [Pt(CH$_2$Ph)Cl(PCH$_2$-ox)] (**1**) and the solvento species [Pt(CH$_2$Ph)(NCMe)(PCH$_2$-ox)]BF$_4$ (**3**·BF$_4$), and **1** and the known [PdMe(NCMe)(PCH$_2$-ox)]-BF$_4$,[6] respectively,[12] consistent in the latter case with a stronger Pt−Cl than Pd−Cl bond in **6**·BF$_4$.

When Ag$^+$ was replaced with Tl$^+$ as chloride abstractor, **4** was not observed. TlCl appeared only in traces, and the main product (**7**) turned out to be an unexpected adduct of Tl$^+$ to **1**, which readily crystallized (Scheme 3). Its X-ray analysis established the formation of both a Pt−Tl bond and a η^6-benzyl−Tl interaction (Figure 2). This bimetallic complex, [(PCH$_2$-ox)ClPtTl{μ-(η^1-CH$_2$;η^6-C$_6$H$_5$)CH$_2$Ph}(*Pt*−*Tl*)]PF$_6$ (**7**·PF$_6$), was also formed when only half an equivalent of TlPF$_6$ was used, illustrating that Tl$^+$ is less reactive than Ag$^+$ toward the Pt−Cl bond, although the bond formation enthalpies for TlCl and AgCl are $\Delta H_f = -204$ and -127 kJ/mol, respectively.[13] Solutions of **7**·PF$_6$ in CH$_2$Cl$_2$ are stable for weeks, but in coordinating solvents, like acetone and acetonitrile, elimination of TlCl occurs immediately with formation of the corresponding solvento species [Pt(CH$_2$-Ph)(PCH$_2$-ox)(solvent)]$^+$.

To our knowledge, **7**·PF$_6$ is the first metal−metal bonded Tl−Pt−Cl complex to be fully characterized.[14] The coordination geometry around Pt(II) is square-pyramidal, with Tl(I) in the apical position (Figure 2). The Pt−Tl distance of 3.0942(9) Å is in the range found for the few other d^8−s^2 Pt(II)−Tl(I) bonds reported in the literature: 2.79−3.14 Å (CSD version 5.25).[15] The metal−metal bond in **7**·PF$_6$ is best described as resulting mainly from donation of electron density from the Pt(II) 5d_{z^2} orbital to the vacant Tl(I) 6p_z orbital.[16] The Pt−Tl bond is not exactly orthogonal to the Pt(II) square-plane (angle of 70(3)°), but parallel to the C(1)−C(2) bond (Figure 2b). This deviation is likely to allow better π-donation from the benzyl ligand to Tl$^+$. The distances between the benzyl carbon atoms C(2)−C(7) and Tl$^+$ are in the range 3.015(5)−3.620(5) Å, so that Tl$^+$ is not perfectly above the centroid of the aromatic ring. The occurrence of both metal−metal and benzyl−Tl$^+$ bonding results in an unprecedented "chelating" behavior for a Pt-benzyl complex. We believe that these interactions are, at least in part, retained in CH$_2$Cl$_2$ solution since no precipitation of TlCl (or TlPF$_6$) was observed. The ^{31}P{^{1}H} NMR spectrum shows no resolved ^2J(P−Tl) coupling and only a minor change in the ^1J(Pt−P) coupling.[15f] No ^1J(Pt−Tl) coupling was detected in the ^{195}Pt{^{1}H} NMR spectrum in CD$_2$Cl$_2$ or CDCl$_3$ solution, and only a broadening of the signal was observed ($\Delta\nu_{1/2}$ ca. 500 Hz). This is consistent with a weak s-character[17] and an important ionic contribution to the Pt−Tl bond and/or a longer Pt−Tl distance in solution, probably for the benefit of a stronger Tl−η^6-benzyl interaction no longer limited by geometrical constraints. The weak intermolecular Tl−F interactions of 2.91(1) and 3.09(1) Å are similar to those in Pt(II)−Tl(I) complexes with C$_6$F$_5$ substituents at the Pt center.[15e] Because no Tl−F coupling was detected in the ^{19}F{^{1}H} NMR at room temperature, it is likely that the ion pair **7**·PF$_6$ is more separate in solution. No significant change in the NMR spectrum was observed down to −80 °C; in particular no diagnostic coupling to Tl was detected. The structural features of **7**·PF$_6$ are different

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(12) When a sample of **5**·BF$_4$ was dissolved in CD$_3$CN, selective irradiation of the PCH$_2$ protons of [Pt(CH$_2$Ph)Cl(PCH$_2$-ox)] (**1**) through homonuclear decoupling showed no effect on the signal of the PCH$_2$ protons of [Pt(CH$_2$Ph)(NCCD$_3$)(PCH$_2$-ox)]$^+$ (**3**), indicating no chemical exchange. Moreover, dissolving equivalent amounts of **1** and **3**·BF$_4$ in CDCl$_3$, in place of CD$_3$CN, did not lead to the formation of **5**·BF$_4$.

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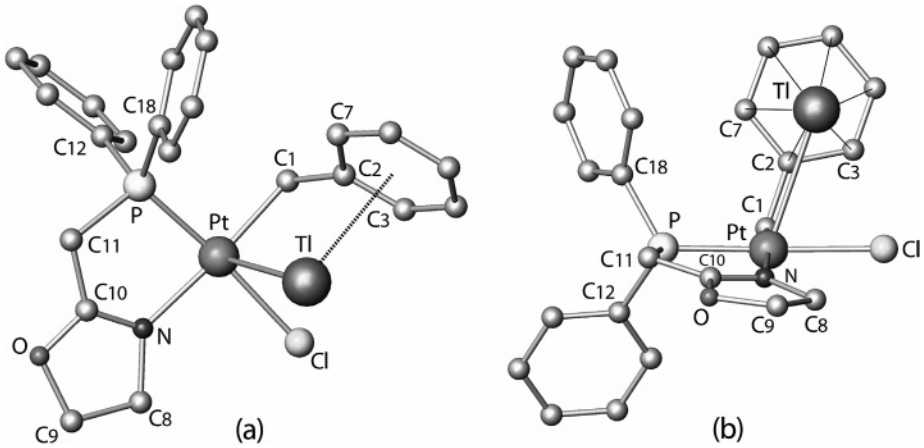
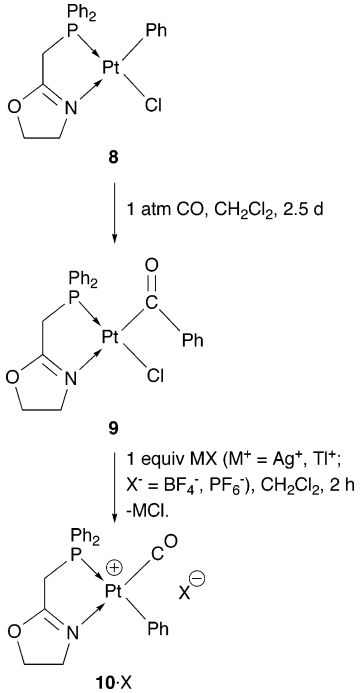


Figure 2. Two views of the molecular structure of **7** in **7**·PF_6. The hydrogen atoms and the counterion have been omitted for clarity. Selected bond distances (Å) and angles (deg): Pt−C1 2.084(5), Pt−N 2.107(4), Pt−P1 2.194(1), Pt−Cl 2.392(2), Pt−Tl 3.0942(9), C1−C2 1.485(7), Tl−C2 3.015(5), Tl−C3 3.111(5), Tl−C4 3.404(5), Tl−C5 3.620(5), Tl−C6 3.555(5), Tl−C7 3.255(5); C1−Pt−P1 93.5(2), N−Pt−P1 83.1(1), C1−Pt−Cl 92.1(2), N−Pt−Cl 91.5(1), C1−Pt−Tl 85.7(1), C2−C1−Pt 114.4(4). There is no significant Tl/Cl interaction, as indicated by a separation of 3.225(5) Å.

from those in a Ru(II) complex that contained TlCl as a ligand but in which the separation of 3.545(2) Å between Ru and Tl was too long to allow significant direct metal−metal interaction.[18] In this complex, two phenyl groups from the tetraphosphine ligand were oriented toward the Tl atom, but the shortest contacts between their carbon atoms and Tl were 3.218(1) and 3.303(1) Å, i.e., much longer than the Tl−C(2) and Tl−C(3) distances in **7**·PF_6.

Scheme 4. Synthesis of 9 and 10



We then considered replacing the benzyl ligand with the structurally related benzoyl ligand, also commonly encountered in organometallic chemistry and homogeneous catalysis,[2a,c−f] which could form a similar Pt−C−C_{ipso}(aryl) angle. Insertion of CO into the Pt−aryl bond

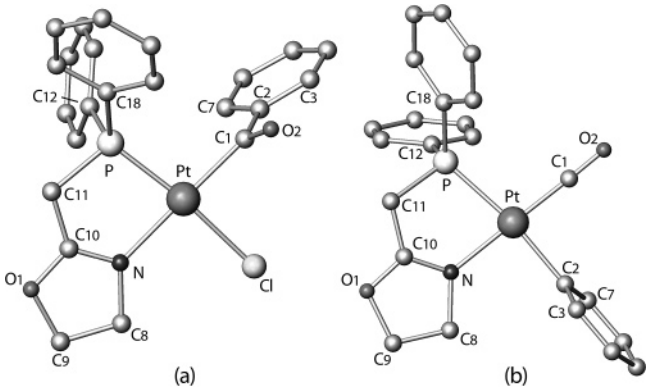


Figure 3. Views of the molecular structures of **9** (a) in **9**·0.5CH_2Cl_2 and of **10** (b) in **10**·PF_6·0.75C_4H_8O. The hydrogen atoms, the counterion, and the solvent have been omitted for clarity. Selected bond distances (Å) and angles (deg) for **9**·0.5CH_2Cl_2: Pt−C1 2.02(1), Pt−N 2.137(9), Pt−P 2.205(3), Pt−Cl1 2.359(3); C1−Pt−P 98.0(3), N−Pt−P 82.6-(2), C1−Pt−Cl1 88.1(3), N−Pt−Cl1 91.4(2), C2−C1−Pt 121(1), Pt−C1−C2−C3 164(1). Selected bond distances (Å) and angles (deg) for **10**·PF_6·0.75C_4H_8O: Pt−C1 1.82(1), Pt−N 2.045(8), Pt−C2 2.07(1), Pt−P1 2.333(3), C1−O2 1.16(1); C1−Pt−C2 88.1(5), N−Pt−C2 91.4(4), C1−Pt−P1 100.0(4), N−Pt−P1 80.7(3), O2−C1−Pt 179(1), Pt−C2−C3−C4−180(1).

of [PtClPh(PCH_2-ox)] (**8**) afforded [Pt{C(O)Ph}Cl(PCH_2-ox)] (**9**) (Figure 3a), which was reacted with MX (M^+ = Ag^+, Tl^+) in CH_2Cl_2. This resulted exclusively in chloride abstraction and CO deinsertion (Scheme 4). That the phenyl ligand in **10** is *trans* to P, in contrast to *trans* to N in **8**, was established by X-ray diffraction (Figure 3b) and results from the respective *trans* influences of the ligands. A comparison of the molecular structures of the benzyl complex **1** and the benzoyl complex **9** shows that although the Pt−C1−C2 angles are similar in both cases (115.9(4)° (**1**), 121(1)° (**9**)), coordination of the aromatic moiety of **9** to a Pt-bound Tl^+ would not be possible due to an unfavorable Pt−C-aryl torsion angle (Pt−C1−C2−C3): 64.7(6)° (**1**), 87.1(5)° (**7**), 164(1)° (**9**). The orientation of the aryl ring in **9** is due to the π-interaction with the carbonyl group.

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Conclusion

Our findings explain why a procedure widely used to abstract a halide ligand in order to generate a positively charged metal complex with enhanced (catalytic) reactivity may not come to full completion or fail owing to either trapping of the cationic complex by the neutral precursor molecule or unexpected "capture" of the Tl(I) cation by the neutral complex acting, in our case, as an unprecedented chelate through metal−metal bond formation and η^6-benzyl coordination. The bonding interaction between the d^8 Pt(II) and s^2 Tl(I) center is assisted by π-donation from the benzyl ligand to the Tl^+ ion. That such interactions were not evidenced in the case of the benzoyl ligand emphasizes the importance of relatively small structural differences (CO vs CH_2) on the reactivity of typical organometallic chloride complexes toward usual halide abstractors. Similar ligand-assisted metallophilic interactions may have a broader scope in reactivity studies and catalysis than previously thought. In this context, it is interesting to note that related alkali metal cation−π interactions involving unsaturated organic moieties continue to attract considerable interest owing to their intrinsic nature and their potential importance in biological systems and for the synthesis of novel molecular devices.[19]

Experimental Section

General Procedures. All manipulations were carried out under inert dinitrogen atmosphere, using standard Schlenk-line conditions and dried and freshly distilled solvents. The ^{1}H, ^{1}H{^{31}P}, ^{13}C{^{1}H}, ^{19}F{^{1}H}, and ^{31}P{^{1}H} NMR spectra were recorded on a Bruker Avance 300 instrument at 300.13, 75.47, 282.40, and 121.49 MHz, respectively, using TMS, $CFCl_3$, or H_3PO_4 (85% in D_2O) as external standards. The ^{195}Pt{^{1}H} NMR spectra were recorded on a Bruker Avance 400 at 86.02 MHz using H_6PtCl_6 in D_2O as external standard. The irradiation experiments on **5**·BF_4 were carried out on a Bruker Avance 500 at 500.13 MHz. All NMR spectra were measured at 298 K, unless otherwise specified. The assignment of the signals was made by ^{1}H,^{1}H-COSY and ^{1}H,^{13}C-HMQC experiments. IR spectra were recorded as KBr pellets on a FT-IR IFS66 Bruker spectrometer. Elemental C, H, and N analyses were performed by the "Service de Microanalyses", Université Louis Pasteur, Strasbourg. ES mass spectra were recorded on a Bruker Daltonics microTOF mass spectrometer.

The ^{1}H NMR spectra of oxazoline systems *N*-coordinated to Pt always show the typical AA′BB′ system for the two methylene groups; the NCH_2 group can additionally show a $^5J_{H-H}$ to the PCH_2 group. When BF_4^- was used as counterion, the ^{19}F{^{1}H} spectra provided the appropriate signal with the pattern typical for ^{10}B−^{19}F and ^{11}B−^{19}F.[20]

The following compounds were synthesized according to literature procedures: [Pt(CH_2Ph)Cl(cod)],[21] [PtClPh(cod)],[21] PCH_2-ox,[6] [Au(PPh_3)Cl],[22] [Cu(NCMe)$_4$]BF_4.[23] Other chemicals were commercially available and used as received. All yields given are based on Pt.

Synthesis and Spectroscopic Data for [Pt(CH_2Ph)Cl(PCH_2-ox)] (1). Solid [Pt(CH_2Ph)Cl(cod)] (0.39 g, 0.91 mmol) and PCH_2-ox (0.25 g, 0.93 mmol) were dissolved in CH_2Cl_2 (20 mL), and the resulting solution was stirred for 3 h at room temperature. Removing all volatiles yielded an off-white residue, which was washed with diethyl ether (2 × 15 mL) and pentane (20 mL) and dried in vacuo to afford the product as a white powder (0.49 g, 0.83 mmol, 91%). Anal. Calcd for $C_{23}H_{23}ClNOPPt$ (590.95): C 46.75, H 3.92, N 2.37. Found: C 46.69, H 3.93, N 2.47. Suitable single crystals for X-ray analysis were obtained at room temperature by slow diffusion of pentane into a solution in CH_2Cl_2/toluene (2:1). ^{1}H NMR (CD_2Cl_2): δ 2.78 (d, 2H, $^3J_{P-H}$ = 4.2 Hz, $^2J_{Pt-H}$ = 100 Hz, PtC*H*$_2$-Ph), 3.22 (dt, 2H, $^2J_{P-H}$ = 10.0 Hz, $^5J_{H-H}$ = 2.0 Hz, $^3J_{Pt-H}$ = 27 Hz, PCH_2), 4.05 (tt, 2H, $^3J_{H-H}$ = 9.7 Hz, $^5J_{H-H}$ = 2.0 Hz, NCH_2), 4.59 (t, 2H, $^3J_{H-H}$ = 9.7 Hz, OCH_2), 6.60−6.70 (m, 2H, *o*-aryl-CH, PtCH_2*Ph*), 6.75−6.85 (m, 3H, *m*-,*p*-aryl-CH, PtCH_2*Ph*), 7.40−7.65 (m, 10H, aryl-CH, PPh_2). ^{1}H NMR ($CDCl_3$): δ 2.88 (d, 2H, $^3J_{P-H}$ = 4.0 Hz, $^2J_{Pt-H}$ = 101 Hz, PtC*H*$_2$Ph), 3.14 (dt, 2H, $^2J_{P-H}$ = 9.9 Hz, $^5J_{H-H}$ = 2.0 Hz, $^3J_{Pt-H}$ = 28 Hz, PCH_2), 4.04 (tt, 2H, $^3J_{H-H}$ = 9.7 Hz, $^5J_{H-H}$ = 2.0 Hz, NCH_2), 4.56 (t, 2H, $^3J_{H-H}$ = 9.7 Hz, OCH_2), 6.78 (br s, 5H, aryl-CH, PtCH_2*Ph*), 7.35−7.60 (m, 10H, aryl-CH, PPh_2). ^{1}H NMR (CD_3CN): δ 2.68 (d, 2H, $^3J_{P-H}$ = 4.1 Hz, $^2J_{Pt-H}$ = 99 Hz, PtC*H*$_2$Ph), 3.33 (dt, 2H, $^2J_{P-H}$ = 10.2 Hz, $^5J_{H-H}$ = 2.0 Hz, $^3J_{Pt-H}$ = 28 Hz, PCH_2), 3.91 (tt, 2H, $^3J_{H-H}$ = 9.7 Hz, $^5J_{H-H}$ = 1.9 Hz, NCH_2), 4.58 (t, 2H, $^3J_{H-H}$ = 9.7 Hz, OCH_2), 6.60−6.70 (m, 2H, aryl-CH, PtCH_2*Ph*), 6.70−6.80 (m, 3H, aryl-CH, PtCH_2*Ph*), 7.45−7.65 (m, 10H, aryl-CH, PPh_2). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 5.8 (d, $^2J_{P-C}$ = 4.1 Hz, $^1J_{Pt-C}$ = 600 Hz, Pt*C*H$_2$Ph), 32.8 (d, $^1J_{P-C}$ = 40.1 Hz, $^2J_{Pt-C}$ = 11 Hz, PCH_2), 52.0 (s, $^2J_{Pt-C}$ = 13 Hz, NCH_2), 72.9 (s, $^3J_{Pt-C}$ = 12 Hz, OCH_2), 122.9 (s, $^5J_{Pt-C}$ = 12 Hz, *p*-aryl-CH, PtCH_2*Ph*), 127.6 (s, $^4J_{Pt-C}$ = 10 Hz, *m*-aryl-CH, PtCH_2*Ph*), 127.8 (d, $^1J_{P-C}$ = 60.9 Hz, *ipso*-aryl, PPh_2), 128.9 (s, $^3J_{Pt-C}$ = 23 Hz, *o*-aryl-CH, PtCH_2*Ph*), 129.2 (d, $^3J_{P-C}$ = 11.8 Hz, *m*-aryl-CH, PPh_2), 132.0 (d, $^4J_{P-C}$ = 2.8 Hz, *p*-aryl-CH, PPh_2), 134.0 (d, $^2J_{P-C}$ = 11.8 Hz, $^3J_{Pt-C}$ = 36 Hz, *o*-aryl-CH, PPh_2), 149.4 (s, $^2J_{Pt-C}$ = 48 Hz, *ipso*-aryl, PtCH_2*Ph*), 175.1 (d, $^2J_{P-C}$ = 13.8 Hz, C=N). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 12.6 (s, $^1J_{Pt-P}$ = 4731 Hz). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 12.9 (s, $^1J_{Pt-P}$ = 4818 Hz). ^{31}P{^{1}H} NMR (CD_3CN): δ 12.1 (s, $^1J_{Pt-P}$ = 4663 Hz). ^{195}Pt{^{1}H} NMR (CD_2Cl_2): δ −3989 (d, $^1J_{P-Pt}$ = 4712 Hz). ^{195}Pt{^{1}H} NMR (CD_3CN): δ −3985 (d, $^1J_{P-Pt}$ = 4640 Hz). IR: 1640 s cm^{-1} ($\nu_{C=N}$).

Synthesis and Spectroscopic Data for [Pt(CH_2Ph)(OTf)(PCH_2-ox)] (2). Solid [Pt(CH_2Ph)Cl(PCH_2-ox)] (**1**) (0.14 g, 0.24 mmol) was dissolved in CH_2Cl_2 (20 mL), and AgOTf (0.07 g, 0.27 mmol) was added in one portion. A white precipitate was formed immediately, and the mixture was stirred at room temperature for 1.5 h. Some Celite was added to the reaction mixture, stirring was continued for 15 min, and the solution was filtered. Removing the solvent in vacuo afforded the product as an off-white powder (0.16 g, 0.23 mmol, 96%). Anal. Calcd for $C_{24}H_{23}F_3NO_4PPtS$ (704.57): C 40.91, H 3.29, N 1.99. Found: C 40.82, H 3.69, N 1.53. ^{1}H NMR ($CDCl_3$): δ 2.76 (s, 2H, $^2J_{Pt-H}$ = 78 Hz, PtC*H*$_2$Ph), 3.55 (d, 2H, $^2J_{P-H}$ = 10.5 Hz, $^3J_{Pt-H}$ = 30 Hz, PCH_2), 4.09 (br t, 2H, $^3J_{H-H}$ = 9.6 Hz, NCH_2), 4.71 (t, 2H, $^3J_{H-H}$ = 9.6 Hz, OCH_2), 6.45−6.55 (m, 2H, aryl-CH, PtCH_2*Ph*), 7.00−7.10 (m, 3H, aryl-CH, PtCH_2*Ph*), 7.60−7.95 (m, 10H, aryl-CH, PPh_2). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 8.2 (br s, PtC*H*$_2$Ph), 31.8 (d, $^1J_{P-C}$ = 45.8 Hz, PCH_2), 53.0 (s, NCH_2), 73.6 (s, OCH_2), 120.5 (br q, $^1J_{F-C}$ = 319.0 Hz, CF_3), 122.0 (br s, *m*-aryl-CH, PtCH_2*Ph*), 125.3 (br s, *p*-aryl-CH, PtCH_2*Ph*), 126.3 (d, $^1J_{P-C}$ = 70.3 Hz, *ipso*-aryl, PPh_2),

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130.1 (br s, *o*-aryl-CH, PtCH$_2$*Ph*), 130.3 (d, $^3J_{P-C}$ = 12.4 Hz, *m*-aryl-CH, PPh$_2$), 133.5 (d, $^4J_{P-C}$ = 2.8 Hz, *p*-aryl-CH, PPh$_2$), 134.0 (d, $^2J_{P-C}$ = 12.5 Hz, $^3J_{Pt-C}$ = 37 Hz, *o*-aryl-CH, PPh$_2$), 146.8 (s, $^2J_{Pt-C}$ = 48 Hz, *ipso*-aryl, PtCH$_2$*Ph*), 175.8 (d, $^2J_{P-C}$ = 11.8 Hz, C=N). ^{19}F{^{1}H} NMR (CDCl$_3$): δ −78.2 (s, OTf). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 8.5 (s, $^1J_{Pt-P}$ = 5204 Hz). IR: 1637 s cm^{-1} ($\nu_{C=N}$).

Synthesis and Spectroscopic Data for [Pt(CH$_2$Ph)(NCMe)(PCH$_2$-ox)]BF$_4$ (3·BF$_4$). Solid [Pt(CH$_2$Ph)Cl(PCH$_2$-ox)] (**1**) (0.21 g, 0.36 mmol) was dissolved in CH$_3$CN (25 mL), and AgBF$_4$ (0.07 g, 0.36 mmol) was added in one portion. A white precipitate was formed immediately, and the mixture was stirred at room temperature for 1.5 h. The solvent was removed in vacuo and the residue extracted with CH$_2$Cl$_2$ (2 × 20 mL). After reducing the volume in vacuo, the product was obtained as an off-white powder by addition of diethyl ether. The elemental analysis proved the formation of a diethyl ether adduct (0.24 g, 0.32 mmol, 89%). Anal. Calcd for C$_{25}$H$_{26}$BF$_4$N$_2$OPPt·C$_4$H$_{10}$O (757.48): C 45.98, H 4.79, N 3.70. Found: C 45.70, H 4.72, N 3.17. ^{1}H NMR (CD$_2$Cl$_2$): δ 1.21 (t, 6H, $^3J_{H-H}$ = 7.0 Hz, OCH$_2$C*H*$_3$, Et$_2$O), 2.30 (br d, 3H, $^5J_{P-H}$ = 0.7 Hz, PtNCC*H*$_3$), 2.67 (d, 2H, $^3J_{P-H}$ = 4.3 Hz, $^2J_{Pt-H}$ = 87 Hz, PtC*H*$_2$-Ph), 3.41 (dt, 2H, $^2J_{P-H}$ = 10.4 Hz, $^5J_{H-H}$ = 2.0 Hz, $^3J_{Pt-H}$ = 26 Hz, PCH$_2$), 3.49 (t, 4H, $^3J_{H-H}$ = 7.0 Hz, OC*H*$_2$CH$_3$, Et$_2$O), 4.08 (tt, 2H, $^3J_{H-H}$ = 9.7 Hz, $^5J_{H-H}$ = 2.0 Hz, NCH$_2$), 4.75 (t, 2H, $^3J_{H-H}$ = 9.7 Hz, OCH$_2$), 6.60−6.70 (m, 2H, *o*-aryl-CH, PtCH$_2$*Ph*), 6.90−7.05 (m, 3H, *m*-,*p*-aryl-CH, PtCH$_2$*Ph*), 7.50−7.80 (m, 10H, aryl-CH, PPh$_2$). ^{1}H NMR (CD$_3$CN): δ 1.98 (br s, 3H, PtNCC*H*$_3$), 2.62 (d, 2H, $^3J_{P-H}$ = 4.2 Hz, $^2J_{Pt-H}$ = 88 Hz, PtC*H*$_2$-Ph), 3.51 (dt, 2H, $^2J_{P-H}$ = 10.6 Hz, $^5J_{H-H}$ = 1.9 Hz, $^3J_{Pt-H}$ = 26 Hz, PCH$_2$), 3.93 (tt, 2H, $^3J_{H-H}$ = 9.7 Hz, $^5J_{H-H}$ = 1.9 Hz, NCH$_2$), 4.67 (t, 2H, $^3J_{H-H}$ = 9.7 Hz, OCH$_2$), 6.50−6.60 (m, 2H, *o*-aryl-CH, PtCH$_2$*Ph*), 6.90−6.95 (m, 3H, *m*-,*p*-aryl-CH, PtCH$_2$*Ph*), 7.55−7.75 (m, 10H, aryl-CH, PPh$_2$). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): δ 3.2 (br s, PtNCC*H*$_3$), 6.3 (d, $^2J_{P-C}$ = 4.8 Hz, $^1J_{Pt-C}$ = 590 Hz, PtCH$_2$Ph), 15.1 (s, OCH$_2$C*H*$_3$, Et$_2$O), 32.2 (d, $^1J_{P-C}$ = 42.9 Hz, PCH$_2$), 53.2 (s, NCH$_2$), 65.9 (s, OCH$_2$CH$_3$, Et$_2$O), 73.8 (s, OCH$_2$), 120.4 (br s, PtNCCH$_3$), 124.0 (s, *p*-aryl-CH, PtCH$_2$*Ph*), 125.8 (d, $^1J_{P-C}$ = 67.1 Hz, *ipso*-aryl, PPh$_2$), 128.2 (s, *m*-aryl-CH, PtCH$_2$*Ph*), 128.3 (s, $^3J_{Pt-C}$ = 21 Hz, *o*-aryl-CH, PtCH$_2$*Ph*), 129.9 (d, $^3J_{P-C}$ = 12.5 Hz, *m*-aryl-CH, PPh$_2$), 133.1 (d, $^4J_{P-C}$ = 2.8 Hz, *p*-aryl-CH, PPh$_2$), 133.8 (d, $^2J_{P-C}$ = 11.8 Hz, $^3J_{Pt-C}$ = 39 Hz, *o*-aryl-CH, PPh$_2$), 147.3 (s, *ipso*-aryl, PtCH$_2$*Ph*), 176.7 (d, $^2J_{P-C}$ = 12.5 Hz, C=N). ^{19}F{^{1}H} NMR (CD$_3$CN): δ −152.2 (BF$_4$). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): δ 10.4 (s, $^1J_{Pt-P}$ = 4802 Hz). ^{31}P{^{1}H} NMR (CD$_3$CN): δ 9.8 (s, $^1J_{Pt-P}$ = 4736 Hz). ^{195}Pt{^{1}H} NMR (CD$_2$Cl$_2$): δ −4194 (d, $^1J_{P-Pt}$ = 4808 Hz). ^{195}Pt{^{1}H} NMR (CD$_3$CN): δ −4198 (d, $^1J_{P-Pt}$ = 4750 Hz). IR: 1637 s cm^{-1} ($\nu_{C=N}$).

Alternatively, cation **3** can also be prepared from TlPF$_6$ or AgOTf instead of AgBF$_4$. **3**·BF$_4$ was also obtained when 1 equiv of [Cu(NCMe)$_4$]BF$_4$ in CH$_2$Cl$_2$/THF was used.

Synthesis and Spectroscopic Data for [Pt(η^3-CH$_2$Ph)(PCH$_2$-ox)]PF$_6$ (4·PF$_6$). Solid [Pt(CH$_2$Ph)Cl(PCH$_2$-ox)] (0.20 g, 0.34 mmol) was dissolved in THF (15 mL), the solution was cooled to −60 °C, and AgPF$_6$ (0.09 g, 0.36 mmol) was added in one portion. The mixture was stirred for 2 h at room temperature, some Celite was added, and the mixture was stirred for an additional 30 min. The solution was then filtered and the solvent removed in vacuo to yield the product as a white powder, which was washed with pentane (20 mL) (0.20 g, 0.29 mmol, 85%). The reaction can also be carried out in CH$_2$Cl$_2$ and with AgBF$_4$ instead of AgPF$_6$. Anal. Calcd for C$_{23}$H$_{23}$F$_6$NOP$_2$Pt (700.46): C 39.44, H 3.31, N 2.00. Found: C 39.05, H 3.83, N 1.66. Further purification by recrystallization led to decomposition of the product, so that no better elemental analysis could be obtained. The product is especially unstable in chlorinated solvents at room temperature. ^{1}H NMR (CDCl$_3$): δ 2.74 (s, 2H, $^2J_{Pt-H}$ = 52 Hz, PtC*H*$_2$Ph), 3.43 (br d, 2H, $^2J_{P-H}$ = 9.6 Hz, $^3J_{Pt-H}$ ≈ 28 Hz, PCH$_2$), 3.94 (br t, 2H, $^3J_{H-H}$ ≈ 10 Hz, NCH$_2$), 4.70 (t, 2H, $^3J_{H-H}$ = 9.6 Hz, OCH$_2$), 6.70−6.90 (br s, 2H, aryl-CH, PtCH$_2$*Ph*), 7.45−7.85 (m, 13H, aryl-CH, PtCH$_2$*Ph* and PPh$_2$). ^{1}H NMR (CD$_2$Cl$_2$): δ 2.81 (s, 2H, $^2J_{Pt-H}$ = 50 Hz, PtC*H*$_2$Ph), 3.44 (br d, 2H, $^2J_{P-H}$ = 10.0 Hz, $^3J_{Pt-H}$ ≈ 28 Hz, PCH$_2$), 3.86 (br t, 2H, $^3J_{H-H}$ ≈ 10 Hz, NCH$_2$), 4.70 (t, 2H, $^3J_{H-H}$ = 9.7 Hz, OCH$_2$), 6.70−6.85 (br s, 2H, aryl-CH, PtCH$_2$*Ph*), 7.25−7.85 (m, 13H, aryl-CH, PtCH$_2$*Ph* and PPh$_2$). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 17.9 (br s, Pt*C*H$_2$Ph), 30.9 (br d, $^1J_{P-C}$ = 41.5 Hz, PCH$_2$), 52.4 (br s, NCH$_2$), 73.1 (s, OCH$_2$), 124−135 (br ms, PtCH$_2$*Ph* and PPh$_2$); C=N could not be assigned. At 188 K, the ^{1}H NMR pattern is not very well resolved owing to dynamic behavior. ^{19}F{^{1}H} NMR (CDCl$_3$): δ −73.3 (d, $^1J_{P-F}$ = 714 Hz, PF$_6$). ^{31}P{^{1}H} NMR (CDCl$_3$): δ ∼28 (br s). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): δ ∼27 (br s, which becomes sharp at 188 K). ^{31}P{^{1}H} NMR (188 K, CD$_2$Cl$_2$): δ 8.7 (s, $^1J_{P-Pt}$ = 5179 Hz). ^{195}Pt{^{1}H} NMR (CDCl$_3$): δ −4052 (d, $^1J_{P-Pt}$ = 5216 Hz). IR: 1640 s cm^{-1} ($\nu_{C=N}$). MS [ES, *m/z* (rel int %)]: 555.1 [M$^+$ − PF$_6$ (100)].

Synthesis and Spectroscopic Data for [{Pt(CH$_2$Ph)(PCH$_2$-ox)}$_2$(μ-Cl)]BF$_4$ (5·BF$_4$). Procedure A. To a solution of [Pt(CH$_2$Ph)Cl(PCH$_2$-ox)] (**1**) (0.36 g, 0.61 mmol) in CH$_2$Cl$_2$ (20 mL) was added AgBF$_4$ (0.06 g, 0.31 mmol) in one portion. The mixture was stirred for 2 h at room temperature, some Celite was added, and the mixture was stirred for additional 30 min. The solution was then filtered and the solvent removed in vacuo to yield **5**·BF$_4$ as an off-white powder. Purification by recrystallization from CH$_2$Cl$_2$/Et$_2$O afforded the product as a CH$_2$Cl$_2$ adduct (0.76 g, 0.58 mmol, 95%). Anal. Calcd for C$_{46}$H$_{46}$BClF$_4$N$_2$O$_2$P$_2$Pt$_2$·CH$_2$Cl$_2$ (1318.18): C 42.83, H 3.67, N 2.13. Found: C 42.65, H 3.88, N 1.85. These crystals were suitable for single-crystal X-ray analysis. ^{1}H NMR (CDCl$_3$): δ 2.83 (d, 2H, $^3J_{P-H}$ = 2.1 Hz, $^2J_{Pt-H}$ = 86 Hz, PtC*H*$_2$Ph), 3.32 (br d, 2H, $^2J_{P-H}$ = 10.2 Hz, PCH$_2$), 3.94 (br t, 2H, $^3J_{H-H}$ = 9.5 Hz, NCH$_2$), 4.56 (t, 2H, $^3J_{H-H}$ = 9.5 Hz, OCH$_2$), 5.30 (s, 2H, CH$_2$Cl$_2$), 6.60−6.70 (br m, 2H, *o*-aryl-CH, PtCH$_2$*Ph*), 6.75−6.85 (br m, 3H, *m*-,*p*-aryl-CH, PtCH$_2$*Ph*), 7.30−7.65 (m, 10H, aryl-CH, PPh$_2$). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 7.2 (br m, Pt*C*H$_2$-Ph), 32.1 (br d, $^1J_{P-C}$ = 42.8 Hz, PCH$_2$), 52.9 (br s, NCH$_2$), 53.4 (s, CH$_2$Cl$_2$), 73.0 (s, OCH$_2$), 123.2 (br s, *p*-aryl-CH, PtCH$_2$*Ph*), 127.6 (br s, *m*-aryl-CH, PtCH$_2$*Ph*), 128.2 (d, $^1J_{P-C}$ = 63.3 Hz, *ipso*-aryl, PPh$_2$), 128.6 (br s, *o*-aryl-CH, PtCH$_2$*Ph*), 129.1 (d, $^3J_{P-C}$ = 11.4 Hz, *m*-aryl-CH, PPh$_2$), 132.2 (br d, $^4J_{P-C}$ = 2.5 Hz, *p*-aryl-CH, PPh$_2$), 133.4 (d, $^2J_{P-C}$ = 11.8 Hz, *o*-aryl-CH, PPh$_2$), 148.2 (br s, *ipso*-aryl, PtCH$_2$*Ph*), 175.0 (br s, C=N). ^{19}F{^{1}H} NMR (CDCl$_3$): δ −154.0 (BF$_4$). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 11.5 (br s, $^1J_{Pt-P}$ = 5209 Hz, PPh$_2$). ^{195}Pt{^{1}H} NMR (CDCl$_3$): δ −4051 (d, $^1J_{P-Pt}$ = 5177 Hz). ^{195}Pt{^{1}H} NMR (193 K, CD$_2$Cl$_2$): δ −4090 (d, $^1J_{P-Pt}$ = 5220 Hz). IR: 1639 s cm^{-1} ($\nu_{C=N}$). MS [ES, *m/z* (rel int %)]: 1146.2 [M$^+$ − BF$_4$ (5)], 555.1 [(C$_{23}$H$_{23}$NOPPt)$^+$ (100)].

When a sample of **5**·BF$_4$ was dissolved in CD$_3$CN, selective irradiation of the PCH$_2$ protons of [Pt(CH$_2$Ph)Cl(PCH$_2$-ox)] (**1**) through homonuclear decoupling showed no effect on the signal of the PCH$_2$ protons of [Pt(CH$_2$Ph)(NCCD$_3$)(PCH$_2$-ox)]$^+$ (**3**).

Procedure B. Cation **5** could also be obtained by using 1 equiv of ZnCl$_2$ in THF,[24] and Zn$_2$Cl$_5^-$ was formed as counterion.[25] The product can be recrystallized from CH$_2$Cl$_2$/pentane. Anal. Calcd for C$_{46}$H$_{46}$ClN$_2$O$_2$P$_2$Pt$_2$·Zn$_2$Cl$_5$·CH$_2$Cl$_2$: C, 36.67; H 3.14; N, 1.82. Found: C, 36.32; H, 3.31; N, 1.64.

Procedure C. Solid [AuCl(PPh$_3$)] (0.14 g, 0.28 mmol) in CH$_2$Cl$_2$ (7 mL) was cooled to −78 °C and AgBF$_4$ (0.06 g, 0.31 mmol) added in one portion. The mixture was stirred for 2 h at −78 °C, and then the precipitate was allowed to settle. The filtered solution of [Au(PPh$_3$)]BF$_4$ was added via cannula to a solution of [Pt(CH$_2$Ph)Cl(PCH$_2$-ox)] (**1**) (0.17 g, 0.29 mmol) in CH$_2$Cl$_2$ (10 mL) at −78 °C. The mixture was stirred for 3 h while kept at this temperature. Removing the solvent in vacuo

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was followed by extraction of the residue at −60 °C with CH_2Cl_2. NMR spectra showed the existence of mixture of [Au(PPh$_3$)]BF_4 and [{Pt(CH_2Ph)(PCH_2-ox)}$_2$(μ-Cl)]BF_4 (**5**·BF_4).

Procedure D. A mixture of equimolar amounts of **1** and **4**·BF_4 in $CDCl_3$ also led to the formation of **5**·BF_4; the reaction was monitored by $^{31}P\{^1H\}$ NMR spectroscopy.

Synthesis and Spectroscopic Data for [{Pt(CH_2Ph)(PCH_2-ox)}(μ-Cl){PdMe(PCH_2-ox)}]BF_4 (6·BF_4). To a solution of [Pt(CH_2Ph)Cl(PCH_2-ox)] (**1**) (0.16 g, 0.27 mmol) in CH_2Cl_2 or THF (15 mL) at −60 °C was added $AgBF_4$ (0.06 g, 0.31 mmol) in one portion. The mixture was stirred for 1.5 h at room temperature, some Celite was added, and the mixture was stirred for an additional 30 min. The solution was then filtered into a solution of [PdMeCl(PCH_2-ox)] (0.12 g, 0.27 mol) in CH_2Cl_2 or THF (15 mL) at −60 °C, and stirring was continued for an additional 2 h. After removing the solvent in vacuo, the residue was extracted with THF (20 mL) and the volume of the solution was reduced again. Addition of diethyl ether afforded a beige powder of the product as a THF adduct (0.26 g, 0.23 mmol, 85%). Anal. Calcd for $C_{40}H_{42}BClF_4N_2O_2P_2PtPd\cdot C_4H_8O$ (1140.60): C 46.33, H 4.42, N 2.46. Found: C 46.60, H 4.57, N 2.33. ^1H NMR ($CDCl_3$): δ 0.55 (s, 3H, PdCH_3), 1.85 (m, 4H, OCH_2CH_2, THF), 2.83 (d, 2H, $^3J_{P-H}$ = 3.5 Hz, $^2J_{Pt-H}$ = 93 Hz, PtCH_2Ph), 3.35 (d, 2H, $^2J_{P-H}$ = 10.3 Hz, PtPCH_2), 3.44 (d, 2H, $^2J_{P-H}$ = 10.6 Hz, PdPCH_2), 3.74 (m, 4H, OCH_2CH_2, THF), 4.01 (br m, 2H, PdNCH_2), 4.20 (br t, 2H, $^3J_{H-H}$ = 9.3 Hz, PtNCH_2), 4.60 (t, 2H, $^3J_{H-H}$ = 9.6 Hz, OCH_2(Pd)), 4.66 (br t, 2H, $^3J_{H-H}$ = 9.3 Hz, OCH_2(Pt)), 6.60−6.75 (br m, 2H, *o*-aryl-CH, PtCH_2*Ph*), 6.75−6.85 (br m, 3H, *m*-,*p*-aryl-CH, PtCH_2*Ph*), 7.35−7.75 (m, 20H, aryl-CH, PPh$_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ −2.5 (s, PdCH_3), 6.8 (br s, PtCH_2Ph), 25.6 (s, OCH_2CH_2, THF), 32.4 (br d, $^1J_{P-C}$ ≈ 39 Hz, PCH_2), 32.5 (d, $^1J_{P-C}$ = 33.2 Hz, PCH_2), 52.6 (br s, NCH_2), 53.1 (s, NCH_2), 68.0 (s, OCH_2CH_2, THF), 72.7 (s, OCH_2), 72.8 (br s, OCH_2), 122.9 (s, *p*-aryl-CH, PtCH_2*Ph*), 127.5 (br s, *m*-aryl-CH, PtCH_2*Ph*), 128.0−133.6 (m, aryl-CH and *ipso*-aryl, PtCH_2*Ph*, PtPPh$_2$ and PdPPh$_2$), 148.6 (br s, *ipso*-aryl, PtCH_2*Ph*), 172.1 (m, C=N(Pd)), 175.2 (m, C=N(Pt)). $^{19}F\{^1H\}$ NMR ($CDCl_3$): δ −154.0 (BF_4). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 11.9 (br s, $^1J_{Pt-P}$ = 5012 Hz, PtPPh$_2$), 34.0 (s, PdPPh$_2$). IR: 1639 s cm^{-1} ($\nu_{C=N}$). MS [ES, *m/z* (rel int %)]: 981.1 [$M^+ - BF_4$ (28)], 555.1 [($C_{23}H_{23}NOPPt)^+$ (30)], 431 (100), 390.0 [($C_{17}H_{19}NOPPd)^+$ (30)].

Synthesis and Spectroscopic Data for [(PCH_2-ox)ClPtTl{μ-(η^1-CH_2;η^6-C_6H_5)CH_2Ph}(*Pt*−*Tl*)]PF_6 (7·PF_6). Solid [Pt(CH_2Ph)Cl(PCH_2-ox)] (**1**) (0.18 g, 0.30 mmol) was dissolved in CH_2Cl_2 (25 mL), and $TlPF_6$ (0.11 g, 0.31 mmol) was added in one portion. The suspension was stirred at room temperature for 2 h, some Celite was added to the reaction mixture (to facilitate removal of traces of TlCl by filtration), and stirring was continued for an additional 15 min. The solution was filtered via cannula and the solvent slowly removed to allow the product to crystallize. (Alternatively, the product can be dissolved in a minimum amount of CH_2Cl_2 (0.5−1 mL) and allowed to crystallize overnight.) It was purified by washing with cold THF (5 mL) and pentane (15 mL), affording an off-white crystalline powder of **7**·PF_6 (0.18 g, 0.19 mmol, 63%). Anal. Calcd for $C_{23}H_{23}ClF_6NOP_2PtTl$ (940.30): C 29.38, H 2.47, N 1.49. Found: C 29.56, H 2.37, N 1.31. Suitable single crystals for X-ray analysis were obtained at room temperature from a CD_2Cl_2 solution in an NMR tube. ^1H NMR (CD_2Cl_2): δ 2.92 (d, 2H, $^3J_{P-H}$ = 4.3 Hz, $^2J_{Pt-H}$ = 96 Hz, PtCH_2Ph), 3.52 (dt, 2H, $^2J_{P-H}$ = 10.4 Hz, $^5J_{H-H}$ = 1.9 Hz, $^3J_{Pt-H}$ = 24 Hz, PCH_2), 4.02 (tt, 2H, $^3J_{H-H}$ = 9.7 Hz, $^5J_{H-H}$ = 1.9 Hz, NCH_2), 4.72 (t, 2H, $^3J_{H-H}$ = 9.7 Hz, OCH_2), 6.44 (br d, 2H, $^3J_{H-H}$ ≈ 7.2 Hz, *o*-aryl-CH, PtCH_2*Ph*), 6.93 (br t, 1H, $^3J_{H-H}$ ≈ 7.2 Hz, *p*-aryl-CH, PtCH_2*Ph*), 7.09 (pseudo t, 2H, $^3J_{H-H}$ ≈ 7.2 Hz, *m*-aryl-CH, PtCH_2*Ph*), 7.60−7.85 (m, 10H, aryl-CH, PPh$_2$). ^1H NMR ($CDCl_3$): δ 2.94 (d, 2H, $^3J_{P-H}$ = 4.3 Hz, $^2J_{Pt-H}$ = 98 Hz, PtCH_2-Ph), 3.44 (br d, 2H, $^2J_{P-H}$ = 10.3 Hz, $^3J_{Pt-H}$ = 23 Hz, PCH_2), 4.11 (br t, 2H, $^3J_{H-H}$ = 9.8 Hz, NCH_2), 4.72 (t, 2H, $^3J_{H-H}$ = 9.8 Hz, OCH_2), 6.60 (br d, 2H, $^3J_{H-H}$ ≈ 7.1 Hz, *o*-aryl-CH, PtCH_2*Ph*), 6.90 (br t, 1H, $^3J_{H-H}$ ≈ 7.2 Hz, *p*-aryl-CH, PtCH_2*Ph*), 7.00 (pseudo t, 2H, $^3J_{H-H}$ ≈ 7.3 Hz, *m*-aryl-CH, PtCH_2*Ph*), 7.50−7.80 (m, 10H, aryl-CH, PPh$_2$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 4.4 (d, $^2J_{P-C}$ = 4.7 Hz, PtCH_2Ph), 32.8 (d, $^1J_{P-C}$ = 42.8 Hz, PCH_2), 52.2 (br s, NCH_2), 73.5 (s, $^3J_{Pt-C}$ = 10 Hz, OCH_2), 124.7 (s, *p*-aryl-CH, PtCH_2*Ph*), 127.1 (d, $^1J_{P-C}$ = 63.9 Hz, *ipso*-aryl, PPh$_2$), 129.1 (s, *m*-aryl-CH, PtCH_2*Ph*), 130.1 (d, $^3J_{P-C}$ = 11.8 Hz, *m*-aryl-CH, PPh$_2$), 130.4 (s, *o*-aryl-CH, PtCH_2*Ph*), 133.1 (br d, $^4J_{P-C}$ = 3.1 Hz, *p*-aryl-CH, PPh$_2$), 133.9 (d, $^2J_{P-C}$ = 11.8 Hz, $^3J_{Pt-C}$ = 34 Hz, *o*-aryl-CH, PPh$_2$), 152.0 (br s, *ipso*-aryl, PtCH_2*Ph*), 176.8 (br s, C=N). $^{19}F\{^1H\}$ NMR (CD_2Cl_2): δ −70.8 (d, $^1J_{P-F}$ = 716 Hz, PF_6). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ −143.0 (sept, $^1J_{P-F}$ = 716 Hz, PF_6), 13.0 (s, $^1J_{Pt-P}$ = 4467 Hz, PPh$_2$). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −143.2 (sept, $^1J_{P-F}$ = 713 Hz, PF_6), 12.7 (s, $^1J_{Pt-P}$ = 4598 Hz, PPh$_2$). $^{195}Pt\{^1H\}$ NMR (CD_2Cl_2): δ −3803 (br d, $^1J_{P-Pt}$ = 4476 Hz). $^{195}Pt\{^1H\}$ NMR ($CDCl_3$): δ ∼−3830 (br d, $^1J_{P-Pt}$ ≈ 4560 Hz). IR: 1637 s cm^{-1} ($\nu_{C=N}$).

Synthesis and Spectroscopic Data for [PtClPh(PCH_2-ox)] (8). A mixture of [PtClPh(cod)] (0.61 g, 1.47 mmol) and PCH_2-ox (0.40 g, 1.49 mmol) was dissolved in CH_2Cl_2 (35 mL), and the resulting solution was stirred for 3 h at room temperature. Removing all volatiles in vacuo yielded the product as an off-white residue, which was washed with diethyl ether (15 mL) and pentane (2 × 15 mL) and dried in vacuo to afford **8** as a white powder (0.82 g, 1.42 mmol, 97%). Anal. Calcd for $C_{22}H_{21}ClNOPPt$ (576.92): C, 45.80; H, 3.67; N, 2.43. Found: C, 45.87; H, 3.92; N, 2.27. ^1H NMR (CD_2Cl_2): δ 3.37 (dt, 2H, $^2J_{P-H}$ = 9.9 Hz, $^5J_{H-H}$ = 2.1 Hz, $^3J_{Pt-H}$ = 24 Hz, PCH_2), 4.17 (tt, 2H, $^3J_{H-H}$ = 9.7 Hz, $^5J_{H-H}$ = 2.1 Hz, NCH_2), 4.71 (t, 2H, $^3J_{H-H}$ = 9.7 Hz, OCH_2), 6.68−6.74 (m, 3H, *m*-, *p*-aryl-CH, PtPh), 6.88−7.08 (m, 2H, $^3J_{Pt-H}$ = 46 Hz, *o*-aryl-CH, PtPh), 7.40−7.60 (ms, 10H, aryl-CH, PPh$_2$). ^1H NMR ($CDCl_3$): δ 3.30 (dt, 2H, $^2J_{P-H}$ = 9.9 Hz, $^5J_{H-H}$ = 2.0 Hz, $^3J_{Pt-H}$ = 24 Hz, PCH_2), 4.24 (tt, 2H, $^3J_{H-H}$ = 9.7 Hz, $^5J_{H-H}$ = 2.0 Hz, NCH_2), 4.68 (t, 2H, $^3J_{H-H}$ = 9.7 Hz, OCH_2), 6.70−6.80 (m, 3H, *m*-,*p*-aryl-CH, PtPh), 6.88−7.08 (m, 2H, $^3J_{Pt-H}$ = 46 Hz, *o*-aryl-CH, PtPh), 7.40−7.60 (ms, 10H, aryl-CH, PPh$_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 31.8 (d, $^1J_{P-C}$ = 39.7 Hz, PCH_2), 51.7 (s, $^2J_{Pt-C}$ = 15 Hz, NCH_2), 72.6 (s, $^3J_{Pt-C}$ = 10 Hz, OCH_2), 122.6 (s, *p*-aryl-CH, PtPh), 127.0 (s, $^3J_{Pt-C}$ = 54 Hz, *m*-aryl-CH, PtPh), 127.8 (d, $^1J_{P-C}$ = 63.3 Hz, *ipso*-aryl, PPh$_2$), 128.8 (d, $^3J_{P-C}$ = 11.2 Hz, *m*-aryl-CH, PPh$_2$), 131.7 (d, $^4J_{P-C}$ = 2.8 Hz, *p*-aryl-CH, PPh$_2$), 133.2 (d, $^2J_{P-C}$ = 11.8 Hz, $^3J_{Pt-C}$ = 34 Hz, *o*-aryl-CH, PPh$_2$), 137.3 (d, $^2J_{Pt-C}$ = 15 Hz, $^3J_{P-C}$ = 3.1 Hz, *o*-aryl-CH, PtPh), 175.5 (d, $^2J_{P-C}$ = 14.3 Hz, C=N); *ipso*-aryl for PtPh not assigned. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 9.5 (s, $^1J_{Pt-P}$ = 4512 Hz). $^{195}Pt\{^1H\}$ NMR (CD_2Cl_2): δ −3850 (d, $^1J_{P-Pt}$ = 4539 Hz). IR: 1643 s cm^{-1} ($\nu_{C=N}$).

Synthesis and Spectroscopic Data for [Pt{C(O)Ph}Cl(PCH_2-ox)] (9). A solution of [PtClPh(PCH_2-ox)] (**8**) (0.26 g, 0.45 mmol) in CH_2Cl_2 (25 mL) was placed under CO atmosphere and stirred for 2.5 days at room temperature. Removing all volatiles in vacuo and purification of the product by filtration through Celite with CH_2Cl_2/toluene (1:1) yielded **9** as a pale yellow residue (0.26 g, 0.43 mmol, 96%). Anal. Calcd for $C_{23}H_{21}ClNO_2PPt$ (604.93): C, 45.67; H, 3.50; N, 2.32. Found: C, 45.45; H, 3.79; N, 2.16. Single crystals suitable for X-ray structure analysis were obtained from toluene/CH_2Cl_2 (1:1), which was layered with pentane. ^1H NMR ($CDCl_3$): δ 3.37 (dt, 2H, $^2J_{P-H}$ = 10.1 Hz, $^5J_{H-H}$ = 2.0 Hz, $^3J_{Pt-H}$ = 27 Hz, PCH_2), 4.13 (tt, 2H, $^3J_{H-H}$ = 9.7 Hz, $^5J_{H-H}$ = 2.0 Hz, NCH_2), 4.68 (t, 2H, $^3J_{H-H}$ = 9.7 Hz, OCH_2), 7.03−7.08 (m, 2H, *m*-aryl-CH, C(O)*Ph*), 7.14−7.20 (m, 1H, *p*-aryl-CH, C(O)*Ph*), 7.29−7.35 (m, 4H, aryl-CH, PPh$_2$), 7.37−7.43 (m, 2H, aryl-CH, PPh$_2$), 7.54−7.61 (m, 4H, aryl-CH, PPh$_2$), 7.76−7.80 (m, 2H, *o*-aryl-CH, C(O)Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 30.8 (d, $^1J_{P-C}$ = 39.7 Hz, $^2J_{Pt-C}$ = 9 Hz, PCH_2), 51.2 (s, $^2J_{Pt-C}$ = 11 Hz, NCH_2), 72.6 (s, OCH_2), 122.6 (s, *p*-aryl-CH, C(O)Ph), 127.0 (s, *o*-aryl-CH, C(O)Ph), 127.9 (d, $^1J_{P-C}$ = 63.0 Hz, *ipso*-aryl, PPh$_2$), 128.8 (d, $^3J_{P-C}$ = 11.4 Hz, *m*-aryl-CH, PPh$_2$), 129.5 (s, *m*-aryl-CH, C(O)*Ph*), 131.6 (d, $^4J_{P-C}$ = 3.0 Hz, *p*-aryl-CH, PPh$_2$), 132.8 (d, $^2J_{P-C}$

= 12.3 Hz, $^3J_{Pt-C}$ = 36 Hz, *o*-aryl-CH, PPh_2), 146.2 (d, $^3J_{P-C}$ = 4.6 Hz, *ipso*-aryl, C(O)*Ph*), 175.0 (d, $^2J_{P-C}$ = 13.7 Hz, C=N), 210.3 (d, $^2J_{P-C}$ = 3.8 Hz, C=O). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 7.0 (s, $^1J_{Pt-P}$ = 4721 Hz). $^{195}Pt\{^1H\}$ NMR ($CDCl_3$): δ −3576 (d, $^1J_{P-Pt}$ = 4703 Hz). IR: 1637 s ($\nu_{C=N}$), 1614 s cm^{-1} ($\nu_{C=O}$).

Synthesis and Spectroscopic Data for [PtPh(CO)(PCH$_2$-ox)]PF$_6$ (10·PF$_6$). A mixture of [Pt{C(O)Ph}Cl(PCH$_2$-ox)] (0.21 g, 0.35 mmol) and $TlPF_6$ (0.13 g, 0.37 mmol) was suspended in CH_2Cl_2 (30 mL), and the mixture was stirred for 2 h at room temperature. Removing all volatiles in vacuo was followed by extraction of the residue with CH_2Cl_2 (15 mL). The product (**10**·PF_6) was obtained as an off-white solid by removing the solvent in vacuo (0.24 g, 0.34 mmol, 97%). Anal. Calcd for $C_{23}H_{21}F_6NO_2P_2Pt$ (714.44): C 38.67, H 2.96, N 1.96. Found: C 38.94, H 3.18, N 1.87. Recrystallization from CH_2Cl_2/THF (2:1) and slow removal of the solvents at room temperature afforded single crystals of **10**·PF_6·0.75C_4H_8O suitable for X-ray analysis. ^1H NMR (CD_2Cl_2): δ 3.48 (tt, 2H, $^3J_{H-H}$ = 9.8 Hz, $^5J_{H-H}$ = 1.7 Hz, NCH_2), 3.88 (dt, 2H, $^2J_{P-H}$ = 10.5 Hz, $^5J_{H-H}$ = 1.7 Hz, PCH_2), 4.74 (t, 2H, $^3J_{H-H}$ = 9.8 Hz, OCH_2), 7.15−7.22 (m, 1H, *p*-aryl-CH, PtPh), 7.29−7.36 (m, 2H, *o*-aryl-CH, PtPh), 7.45−7.80 (ms, 12H, aryl-CH, PtPh and PPh_2). $^1H\{^{31}P\}$ NMR (CD_2Cl_2): δ 3.48 (tt, 2H, $^3J_{H-H}$ = 9.8 Hz, $^5J_{H-H}$ = 1.7 Hz, NCH_2), 3.87 (br s, 2H, PCH_2), 4.74 (t, 2H, $^3J_{H-H}$ = 9.8 Hz, OCH_2), 7.15−7.22 (m, 1H, *p*-aryl-CH, PtPh), 7.30−7.35 (m, 2H, aryl-CH, PtPh), 7.45−7.80 (m, 12H, aryl-CH, PtPh and PPh_2). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 29.4 (d, $^1J_{P-C}$ = 41.7 Hz, $^2J_{Pt-C}$ = 15 Hz, PCH_2), 52.5 (d, $^4J_{P-C}$ = 2.1 Hz, $^2J_{Pt-C}$ = 59 Hz, NCH_2), 74.5 (s, $^3J_{Pt-C}$ = 35 Hz, OCH_2), 125.8 (d, $^1J_{P-C}$ = 54.8 Hz, *ipso*-aryl, PPh_2), 126.7 (br s, $^4J_{Pt-C}$ = 7 Hz, *p*-aryl-CH, PtPh), 130.2 (d, $^2J_{P-C}$ = 16.9 Hz, $^2J_{Pt-C}$ = 44 Hz, *o*-aryl-CH, PtPh), 130.5 (d, $^3J_{P-C}$ = 11.7 Hz, *m*-aryl-CH, PPh_2), 133.0 (d, $^4J_{P-C}$ = 13.1 Hz, $^3J_{Pt-C}$ = 13 Hz, *m*-aryl-CH, PtPh), 133.3 (d, $^4J_{P-C}$ = 2.8 Hz, *p*-aryl-CH, PPh_2), 136.0 (d, $^2J_{P-C}$ = 2.8 Hz, $^3J_{Pt-C}$ = 24 Hz, *o*-aryl-CH, PPh_2), 144.1 (d, $^2J_{P-C}$ = 46.7 Hz, $^1J_{Pt-C}$ = 641 Hz, *ipso*-aryl, PtPh), 165.1 (d, $^2J_{P-C}$ = 6.9 Hz, $^1J_{Pt-C}$ = 1827 Hz, C=O), 188.1 (d, $^2J_{P-C}$ = 23.5 Hz, $^2J_{Pt-C}$ = 46 Hz, C=N). $^{19}F\{^1H\}$ NMR (CD_2Cl_2): δ −73.4 (d, $^1J_{P-F}$ = 712 Hz, PF_6). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ −143.3 (sept, $^1J_{P-F}$ = 712 Hz, PF_6), 25.8 (s, $^1J_{Pt-P}$ = 1390 Hz, PPh_2). $^{195}Pt\{^1H\}$ NMR (CD_2Cl_2): δ −4256 (br d, $^1J_{P-Pt}$ = 1371 Hz). IR: 2091 s ($\nu_{C=O}$) cm^{-1}, 1641 w, 1614 ms cm^{-1}.

Cation **10** can also be prepared from **9** and 1 equiv of $AgBF_4$ or 1 equiv of [Au(PPh_3)]BF_4 in CH_2Cl_2 to yield **10**·BF_4.

X-ray Crystal Structure Determination of 1, 5·BF$_4$·0.5CH$_2$Cl$_2$, 7·PF$_6$, 9·0.5CH$_2$Cl$_2$, and 10·PF$_6$·0.75C$_4$H$_8$O. The diffraction data were collected on a Nonius Kappa-CCD area detector diffractometer (Mo Kα, λ = 0.71070 Å; phi scan) at T = 173(2) K. The complete conditions of the data collection (Denzo software) and structural refinements are given below. The cell parameters were determined from reflections taken from one set of 10 frames (1.0° steps in phi angle), each at 20 s exposure. The structures were solved using direct methods (SHELXS97) and refined against F^2 using the SHELXL97 software. The absorption was corrected empirically (with Sortav)[26a] for compounds **1**, **5**·BF_4·0.5CH_2Cl_2, **7**·PF_6, and **9**·0.5CH_2Cl_2. Largest peaks are near the Pt atoms (at 0.88 and 0.92 Å). All non-hydrogen atoms were refined anisotropically unless otherwise specified. Hydrogen atoms were generated according to stereochemistry and refined using a riding model in SHELXL97.[26b]

Complex 1: $C_{23}H_{23}ClNOPPt$; M = 590.93; monoclinic, $P2_1/a$; a = 16.103(2) Å, b = 8.642(1) Å, c = 17.032(2) Å, β = 114.11(5)°; V = 2163.4(4) Å^3, Z = 4, D_c = 1.814 g cm^{-3}, μ = 6.697 mm^{-1}, F(000) = 1144; $T_{min/max}$ = 0.318/0.408. Colorless prisms, dimensions 0.14 × 0.13 × 0.11 mm^3; total number of collected reflections 9400 (independent 9399), with 6804 having $I > 2\sigma(I)$; 2.62° < θ < 34.96°; 253 parameters. Final results: R1 = 0.0511; wR2 = 0.1392, Gof = 1.001, max./min. residual electronic density = 4.548/−3.877 e Å^{-3}.

Complex 5·BF$_4$·0.5CH$_2$Cl$_2$: $C_{46}H_{46}BClF_4N_2O_2P_2Pt_2$·0.5$CH_2Cl_2$; M = 1275.69; monoclinic, $P2_1/n$; a = 16.000(1) Å, b = 13.307(2) Å, c = 23.089(2) Å, β = 94.49(4)°; V = 4900.8(9) Å^3, Z = 4, D_c = 1.729 g cm^{-3}, μ = 5.930 mm^{-1}, F(000) = 2468; $T_{min/max}$ = 0.730/0.893. Colorless prisms, dimensions 0.08 × 0.07 × 0.05 mm^3; total number of collected reflections 38 110 (independent 14 301), with 8787 having $I > 2\sigma(I)$; 1.50° < θ < 30.05°; 568 parameters. Final results: R1 = 0.0700; wR2 = 0.1820, Gof = 1.044, max./min. residual electronic density = 1.023/−1.102 e Å^{-3}.

Complex 7·PF$_6$: $C_{23}H_{23}ClF_6NOP_2PtTl$; M = 940.27; triclinic, $P\bar{1}$; a = 8.864(1) Å, b = 11.287(1) Å, c = 13.984(1) Å, α = 80.83(3)°, β = 72.74(3)°, γ = 84.38(3)°; V = 1317.1(2) Å^3, Z = 2, D_c = 2.371 g cm^{-3}, μ = 11.698 mm^{-1}, F(000) = 872; $T_{min/max}$ = 0.214/0.339. Colorless needles, dimensions 0.12 × 0.10 × 0.11 mm^3; total number of collected reflections 9064 (independent 6017), with 5346 having $I > 2\sigma(I)$; 1.54° < θ < 27.46°; 325 parameters. Final results: R1 = 0.0284; wR2 = 0.0920, Gof = 1.209, max./min. residual electronic density = 0.901/−2.403 e Å^{-3}.

Complex 9·0.5CH$_2$Cl$_2$: $C_{23}H_{21}ClNO_2PPt$·0.5CH_2Cl_2; M = 647.38; monoclinic, $P2_1/a$; a = 11.094(1) Å, b = 12.717(1) Å, c = 16.605(1) Å, β = 104.04(5)°; V = 2272.7(3) Å^3, Z = 4, D_c = 1.892 g cm^{-3}, μ = 6.501 mm^{-1}, F(000) = 1252, $T_{min,max}$ = 0.574/0.602. Pale yellow prisms, dimensions 0.08 × 0.07 × 0.07 mm^3; total number of collected reflections 11 590 (independent 6631), with 3687 having $I > 2\sigma(I)$; 1.26° < θ < 30.02°; 270 parameters. Final results: R1 = 0.1201; wR2 = 0.1404, Gof = 1.119, max./min. residual electronic density = 2.43/−1.86 e Å^{-3}. The heavy atoms of the solvent molecules have only been refined isotropically. A disordered CH_2Cl_2 molecule (occupancy factor = 0.5) was found near to the −1 symmetry center (0,0,0.5), which could account for the relatively large wR2 value.

Complex 10·PF$_6$·0.75C$_4$H$_8$O: $C_{23}H_{21}F_6NO_2P_2Pt$·0.75C_4H_8O; M = 768.52; orthorhombic, $P2_122_1$; a = 9.849(1) Å, b = 12.830(3) Å, c = 22.661(5) Å; V = 2864(1) Å^3, Z = 4, D_c = 1.783 g cm^{-3}, μ = 5.078 mm^{-1}, F(000) = 1496. Off-white prisms, dimensions 0.08 × 0.07 × 0.07 mm^3; total number of collected reflections 25 904 (independent 6565), with 5301 having $I > 2\sigma(I)$; 1.59° < θ < 27.47°; 334 parameters. Final results: R1 = 0.0550; wR2 = 0.1311, Gof = 1.033, max./min. residual electronic density = 1.712/−1.912 e Å^{-3}; Flack parameter 0.004(13). The heavy atoms of the solvent molecules have only been refined isotropically, leading to one residue corresponding to a THF molecule with occupancy factor 0.5 and another THF molecule with occupancy factor 0.25.

Crystallographic data for these structures have been deposited with the Cambridge Crystallographic Data Centre as Supplementary Publication nos. CCDC 241929−241933. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Supporting Information Available: ORTEP plots for the metal complex part of **1**, **5**·BF_4·0.5CH_2Cl_2, **7**·PF_6, **9**·0.5CH_2Cl_2, and **10**·PF_6·0.75C_4H_8O; crystallographic data are available as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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