Heterobimetallic Complexes

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Reversible Insertion of Platinum into Coinage Group Metal–Halogen Bonds**

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Insertion of transition-metal (TM) complexes into element–halogen bonds is one of the basic concepts in TM chemistry. The most common examples are found for main-group species such as alkyl[1–3] and boryl halides.[4–7] Here, the insertion proceeds with oxidation of the TM and thus constitutes an oxidative addition (OA) process, which is a crucial step in TM-mediated catalysis. Another possibility, albeit much less common, is the insertion of a main-group metal such as tin into TM–halogen bonds, which does not affect the oxidation state of the TM.[8–11] In the present work we focus on the combination of these two reaction patterns, that is, the insertion of a TM into a TM–halogen bond; this constitutes a versatile route to heterodinuclear TM complexes containing platinum and a coinage metal.

There have been numerous investigations into the bonding properties of homo- and heterodinuclear transition-metal complexes. Among the earliest examples were homodinuclear complexes consisting of d^8–d^8 as well as d^{10}–d^{10} systems (type **B**, Figure 1).[12–15] However, the combination of platinum and gold is exclusively found in mixed-valence systems, such as d^8–d^{10} (type **A**) and d^7–d^9;[16–19] in contrast, the route presented herein leads to heterodinuclear d^{10}–d^{10} complexes. In addition, the most striking feature of nearly all known compounds of this type is the chelating ligand forcing the two transition metals to interact. Again this stands in stark contrast to the compounds presented in this work that contain *unsupported* TM–TM bonds without a bridging ligand.

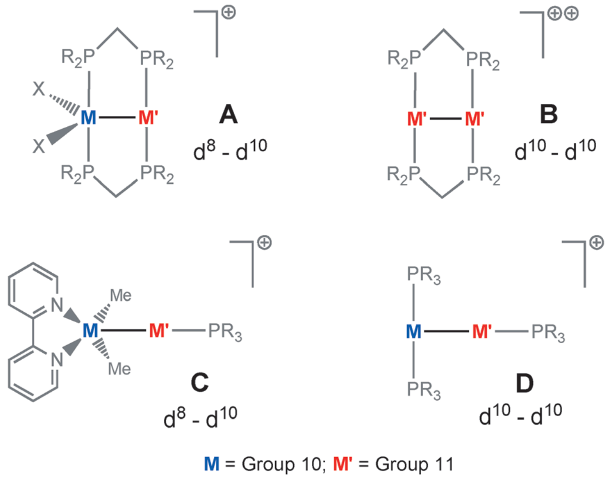

Figure 1. Selected bimetallic structural motifs relevant to the current work.

While unsupported bonds are relatively uncommon,[20] a few examples of complexes having d^8–d^{10} interactions should be mentioned (type **C**).[21] To the best of our knowledge, the only complex featuring an unsupported d^{10}–d^{10} interaction (type **D**) between platinum and a coinage-group metal was reported by Sharp et al. in 1998.[22] However, no signs of an insertion reaction were detected at that time.

In contrast, in our synthetic approach we use the well-established transition-metal Lewis base $[(Cy_3P)_2Pt]$ (**1**) and the gold complex $[(Cy_3P)AuCl]$ (**2**). We describe the unprecedented reversible insertion of the Lewis basic platinum fragment into a coinage-metal–halogen bond. The insertion products were investigated by multinuclear NMR spectroscopy and single-crystal X-ray diffraction. In addition, we present a possible mechanism for the insertion reaction supported by density functional calculations.

The reaction of the sterically and electronically unsaturated platinum compound $[(Cy_3P)_2Pt]$ (**1**) with an equimolar amount of $[(Cy_3P)AuCl]$ (**2**) leads instantly to an equilibrium of the two starting materials with a new complex **3**, as indicated by $^{31}P\{^1H\}$ NMR spectroscopic data. The resonances of **1** ($\delta = 62.2$ ppm), flanked by ^{195}Pt satellites ($J = 4155$ Hz), and **2** ($\delta = 53.1$ ppm) are accompanied by the resonances of **3** at $\delta = 42.7$ ppm ($J = 3157$ Hz) and $\delta = 38.2$ ppm ($J = 1295$ Hz). The appearance of ^{195}Pt satellites in both of the latter resonances suggests a heterobimetallic compound in which the smaller coupling constant of 1295 Hz presumably indicates a ^2J coupling.

Further information about the constitution of **3** in solution was gained from the ^{195}Pt NMR spectrum. In addition to the resonance of **1** ($\delta = -6505$ ppm) a resonance at $\delta = -4531$ ppm was detected as a triplet ($J = 3157$ Hz) of doublets ($J = 1295$ Hz). We therefore propose the formula *trans*-$[Cl(Cy_3P)_2PtAu(PCy_3)]$ for compound **3** (see Table 1). The ratio between the new complex and the starting materials is almost 1:1, but adding **2** in excess shifts the equilibrium towards **3**.

Reaction of the related bromo complex $[(Cy_3P)AuBr]$ (**4**) with **1** leads to the analogous heterobimetallic complex *trans*-$[Br(Cy_3P)_2PtAu(PCy_3)]$ (**5**). Accordingly, the resonances in the $^{31}P\{^1H\}$ NMR spectra are located in the same region and the ^{195}Pt NMR coupling constants are of similar magnitude ($\delta = 42.0$ ppm, $J = 3161$ Hz and $\delta = 36.2$ ppm, $J = 1345$ Hz).

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Table 1: $^{31}P\{^1H\}$ NMR parameters of compounds **1**–**5**.

	$^{31}P_{(P\text{-}Pt)}$[a]	$^{31}P_{(P\text{-}Au)}$[a]	$^{1}J_{Pt\text{-}P}$[b]	$^{2}J_{Pt\text{-}P}$[b]
1	62.2	–	4155	–
2	–	53.1	–	–
3	42.7	38.2	3157	1295
4	–	57.3	–	–
5	42.0	36.2	3161	1345

[a] δ in ppm. [b] Coupling constants in Hz.

Here, the equilibration seems to be much faster than in the case of the chloro complex **3**, as judged by the very broad resonances in the $^{31}P\{^1H\}$ NMR spectrum (see Table 1). The existence of an equilibrium, and consequently the reversibility of the insertion, was further supported by control experiments.[23] Moreover, variable-temperature (VT) NMR experiments were performed to determine the equilibrium constant at different temperatures. Thus, at −30 °C, only the insertion product **3** was observed, whereas at 70 °C only the starting materials **1** and **2** were detectable.

Single crystals of **3** and **5** suitable for X-ray diffraction analyses were obtained from saturated solutions in fluorobenzene at ambient temperature. Both complexes display square-planar coordination at the platinum and a linear arrangement at the gold center. In both complexes the halogen atom is located in *trans* position with respect to the gold fragment, indicating an insertion of the Lewis basic platinum fragment into the gold–halogen bond (Figure 2).

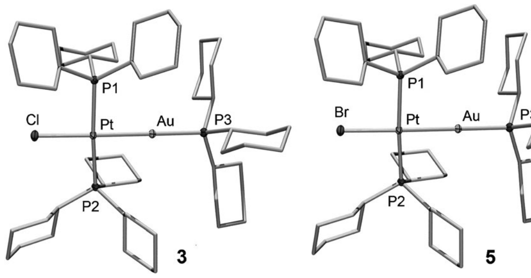

Figure 2. Molecular structures of *trans*-[Cl(Cy$_3$P)$_2$PtAu(PCy$_3$)] (**3**) and *trans*-[Br(Cy$_3$P)$_2$PtAu(PCy$_3$)] (**5**). Relevant bond lengths [Å] and angles [°]: **3**: Pt–Au 2.569(1), Pt–Cl 2.494(1); Pt-Au-P3 176.0(1), P1-Pt-P2 172.2(1), Cl-Pt-Au 176.5(1); **5**: Pt–Au 2.600(1), Pt–Br 2.634(1); Pt-Au-P3 177.7(1), P1-Pt-P2 168.4(1), Br-Pt-P1 178.6(1). Ellipsoids drawn at the 50% probability level; ellipsoids for the ligands, hydrogen atoms, and solvent molecules omitted for clarity.

In analogy to studies on somewhat related platinum boryl complexes such as *trans*-[Br(Cy$_3$P)$_2$Pt(BBr$_2$)] (**6**),[24] we attempted to abstract the halide from the platinum fragment in order to obtain T-shaped complexes. Indeed, addition of one equivalent of Na[B(C$_8$H$_3$Cl$_2$)$_4$] in a polar solvent like fluorobenzene yields the T-shaped complex *trans*-[(Cy$_3$P)$_2$PtAu(PCy$_3$)][B(C$_8$H$_3$Cl$_2$)$_4$] (**7**). Resonances in the $^{31}P\{^1H\}$ NMR spectrum are located at $\delta = 60.4$ ppm flanked by ^{195}Pt satellites ($J = 3005$ Hz) and at $\delta = 29.6$ ppm ($J = 1709$ Hz). Interestingly, the $^3J_{P\text{-}P}(cis)$ coupling is resolved, in contrast to **3** and **5**; therefore the signal at $\delta = 60.4$ ppm for the two equivalent PCy$_3$ ligands bound to platinum appears as a doublet ($J = 3$ Hz), whereas the resonance of the PCy$_3$ group bound to gold at $\delta = 29.6$ ppm is a triplet ($J = 3$ Hz). In the ^{195}Pt NMR spectrum a triplet ($J = 3005$ Hz) of doublets ($J = 1709$ Hz) is detected at $\delta = -4619$ ppm. Further verification of the proposed structure of **7** was obtained by single-crystal X-ray diffraction (Figure 3).

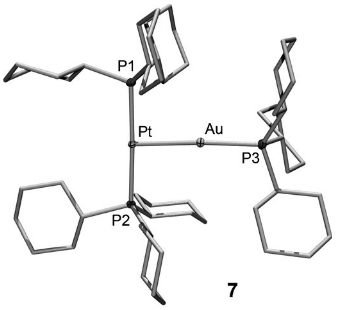

Figure 3. Molecular structure of *trans*-[(Cy$_3$P)$_2$PtAu(PCy$_3$)][B(C$_6$H$_3$Cl$_2$)$_4$] (**7**). Relevant bond lengths [Å] and angles [°]: Pt–Au 2.541(1); Pt-Au-P3 175.3(1), P1-Pt-P2 176.6(1). Ellipsoids drawn at the 50% probability level; ellipsoids for the ligands, the [B(C$_6$H$_3$Cl$_2$)$_4$] counterion, hydrogen atoms, and solvent molecules omitted for clarity.

In order to investigate the reactivity of the lighter coinage metals, the complexes [(Cy$_3$P)AgCl] (**8**) and [(Cy$_3$P)CuCl] (**9**) were treated with equimolar amounts of [(Cy$_3$P)$_2$Pt] (**1**). Notably, monitoring of the reactions by NMR spectroscopy indicated no formation of *trans*-[Cl(Cy$_3$P)$_2$PtAg(PCy$_3$)] (**10**) or *trans*-[Cl(Cy$_3$P)$_2$PtCu(PCy$_3$)] (**11**), presumably because of the poor solubility of **8** and **9** (even in fluorobenzene) in contrast to **3** and **5**. However, addition of one equivalent of Na[B(C$_6$H$_3$Cl$_2$)$_4$] to the reaction mixtures of **1** and **8** or **9** yielded the T-shaped complexes *trans*-[(Cy$_3$P)$_2$PtAg(PCy$_3$)][B(C$_8$H$_3$Cl$_2$)$_4$] (**12**) and *trans*-[(Cy$_3$P)$_2$PtCu(PCy$_3$)][B(C$_8$H$_3$Cl$_2$)$_4$] (**13**), respectively. The resonances in the $^{31}P\{^1H\}$ NMR spectra are similar to those of **7**. For example, **12** gives rise to two sets of resonances, one located at $\delta = 62.7$ ppm for the platinum-bound phosphines (flanked by ^{195}Pt satellites with a coupling constant of 3092 Hz) split into a doublet of doublets due to $^3J_{P\text{-}P}$ and $^2J_{Ag\text{-}P}$ coupling (2 Hz, respectively) and the other one at $\delta = 32.2$ ppm. The latter resonance appears as two separate doublets ($J = 502$ Hz for the isotope ^{107}Ag and $J = 579$ Hz for ^{109}Ag) each split into a triplet due to the $^3J_{P\text{-}P}$ coupling (3 Hz). In addition, ^{195}Pt satellites were detected with a $^2J_{Pt\text{-}P}$ coupling constant of 1018 Hz (see Table 2). In contrast, in the $^{31}P\{^1H\}$ NMR spectrum of **13** the coupling to copper ($I = 3/2$ for both ^{63}Cu and ^{65}Cu) is not resolved, and only two broad resonances are

Table 2: $^{31}P\{^1H\}$ NMR parameters of compounds **7**, **12**, and **13**.

	$^{31}P_{(P\text{-}Pt)}$[a]	$^{31}P_{(P\text{-}M)}$[a,b]	$^{1}J_{Pt\text{-}P}$[c]	$^{2}J_{Pt\text{-}P}$[c]
7	60.4	29.6	3005	1709
12	62.7	32.2	3092	1018
13	62.1	19.5	3091	918

[a] δ in ppm. [b] M = Au, Ag, Cu. [c] Coupling constants in Hz.

found at $\delta = 62.1$ ppm ($^1J_{\text{Pt-P}} = 3091$ Hz) and 19.5 ppm ($^2J_{\text{Pt-P}} = 918$ Hz).

X-ray diffraction analyses of the three T-shaped compounds **7**, **12**, and **13** reveal a strong resemblance. They all crystallize in the triclinic space group $P\bar{1}$ and the platinum–metal distances increase with the covalent radii of the coinage metals by about 15 pm from copper (239.4(1) pm) to gold (254.1(1) pm) and further 3 pm to silver (256.6(1) pm); see Figure 4).

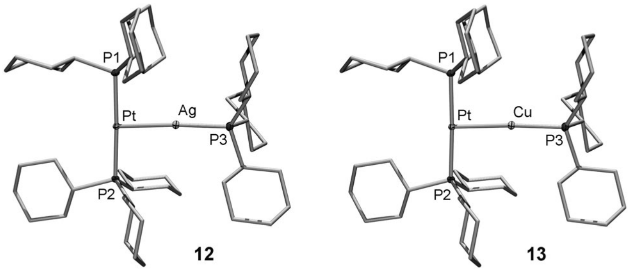

Figure 4. Molecular structures of *trans*-$[(Cy_3P)_2PtAu(PCy_3)][B(C_6H_3Cl_2)_4]$ (**12**) *trans*-$[(Cy_3P)_2PtAu(PCy_3)][B(C_8H_3Cl_2)_4]$ (**13**). Relevant bond lengths [Å] and angles [°]: **12**: Pt–Ag 2.566(1); Pt-Ag-P3 174.3(1), P1-Pt-P2 174.7(1); **13**: Pt–Cu 2.394(1); Pt-Cu-P3 176.3(1), P1-Pt-P2 174.4(1). Ellipsoids drawn at the 50% probability level; ellipsoids for the ligands, the $[B(C_6H_3Cl_2)_4]$ counterion, hydrogen atoms, and solvent molecules omitted for clarity.

To gain deeper insight into the mechanism of the insertion reaction, we performed density functional theory (DFT) calculations.[23] To reduce computational costs, cyclohexyl groups were exchanged for methyl groups. Initially, the electronic energies of the reactions of $[(Me_3P)_2Pt]$ (**1′**) with $[(Me_3P)AuCl]$ (**2′**), $[(Me_3P)AuBr]$ (**4′**), $[(Me_3P)AgCl]$ (**8′**), and $[(Me_3P)CuCl]$ (**9′**) were determined by comparison of the SCF energies of the starting materials and the reaction products. The formation of $[Cl(Me_3P)_2PtAu(PMe_3)]$ (**3′**) has the most negative energy (-47 kJ mol^{-1}), closely followed by the bromo complex $[Br(Me_3P)_2PtAu(PMe_3)]$ (**5′**) with -46 kJ mol^{-1}. The reaction energies of $[Cl(Me_3P)_2PtAg(PMe_3)]$ (**10′**, -20 kJ mol^{-1}) and $[Cl(Me_3P)_2PtCu(PMe_3)]$ (**11′**, 1 kJ mol^{-1}) are much smaller. These findings are in accord with the experiments, where the insertion products of silver and copper were not detected. Additionally in the case of the gold complex, the calculated electronic energy is in surprisingly good agreement with that determined experimentally by VT NMR spectroscopy for the formation of **3** (also 47 kJ mol^{-1}).[23]

Additionally, the electronic ground state structures of the cationic species $[(Me_3P)_2PtAu(PMe_3)]^+$ (**7′**), $[(Me_3P)_2PtAg(PMe_3)]^+$ (**12′**), and $[(Me_3P)_2PtCu(PMe_3)]^+$ (**13′**) were calculated. The degree of orbital interactions was estimated by the natural bond orbital (NBO) method. Apparently, halide abstraction has no pronounced influence on the Wiberg bond indices (WBI) of the Pt–M bonds (M = Cu, Ag, Au). However, analysis of the natural charges is more meaningful. Here, the negative charge at the platinum center increases with decreasing electronegativity of the coinage metal (i.e. from Cu to Au). The neutral species display, according to this trend, a small charge separation between the platinum and the other metals (**3′**: Δ0.04, **5′**: Δ0.12; **10′**: Δ0.37, **11′**: Δ0.46). In contrast, the cationic species show a distinct separation. The lowest is found for platinum and gold (**7′**, Δ0.53), followed by silver (**12′**, Δ0.84) and copper (**13′**, Δ0.86; see Table 3). The negatively charged platinum center is therefore comparable with the platinum in neutral metal-only Lewis pairs (MOLPs),[25] for example $[(Cy_3P)_2Pt(AlCl_3)]$ (**14**, -0.31),[25] suggesting that the coinage-group-metal fragment acts as a Lewis acid in the title compounds. To further support the description of the cationic complexes as MOLPs, orbital interactions were analyzed. The bond between the two TMs can be regarded as the donating of electron density from a HOMO of the platinum to the LUMO of the gold fragment.[23] However, the most significant evidence is given by the reaction of **7**, **12**, and **13** with one equivalent of PCy_3, which yields in all cases the neutral platinum(0) complex $[(Cy_3P)_2Pt]$ (**1**) and the cationic bis(phosphine) coinage-metal compounds (determined by $^{31}P\{^1H\}$ NMR spectroscopy).[23]

Table 3: Selected calculated parameters.

	3′	**5′**	**10′**	**11′**
WBI[a] (Pt-M)[b]	0.45	0.44	0.46	0.45
nat. charge Pt	−0.08	−0.11	−0.17	−0.20
nat. charge M[b]	−0.04	0.01	0.20	0.26
	14	**7′**	**12′**	**13′**
WBI[a] (Pt-M)[b]	–	0.41	0.38	0.37
nat. charge Pt	−0.31	−0.32	−0.40	−0.41
nat. charge M[b]	–	0.21	0.44	0.45

[a] Wiberg bond index. [b] M = Au, Ag, Cu.

In conclusion, we have described the reversible insertion of the transition-metal complex $[(Cy_3P)_2Pt]$ (**1**) into gold—halogen bonds, along with spectroscopic characterization by multinuclear NMR experiments, elemental analyses, single-crystal X-ray diffraction analyses, and theoretical investigations. Furthermore, we have synthesized three unsupported heterobimetallic complexes which also can be regarded as metal-only Lewis pairs (MOLPs), and thus provide a convenient route to mixed d^{10}–d^{10} complexes.

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[23] Experimental procedures, details on the X-ray diffraction and theoretical studies, and analytical data of all compounds are provided in the Supporting Information. CCDC 890995 (**3**), 890996 (**5**), 890997 (**7**), 890998 (**12**), 890999 (**13**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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