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Transmetalation Supported by a Pt^{II}–Cu^{I} Bond**

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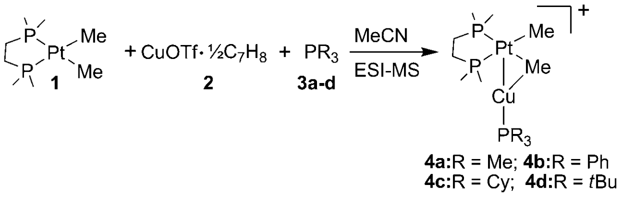
Transmetalation reactions are thought to be key steps in cross-coupling reactions catalyzed by late transition metals.[1] For example, the widely used copper-cocatalyzed Sonogashira coupling reaction is believed to involve the transfer of an alkynyl group from copper(I) to palladium(II).[2] Despite their importance, detailed mechanistic information and reliable thermochemical data on these elementary reactions are scarce. It is thus desirable to observe and manipulate the bimetallic intermediates from which they occur. Along these lines, the group of Osakada[3a–c] reported hydroxy-bridged dinuclear phenylplatinum(II) complexes that undergo anion-induced transmetalation. In addition, Komiya[3d–f] reported several heterobimetallic complexes promoting methyl or aryl group transfer from platinum; these reactions are best described as reductive eliminations involving the reduction of Pt^{II} to Pt^{0} or of Pt^{IV} to Pt^{II}.

Heterometallic organic-group transfer involving d^8 and d^{10} centers[3g–i] are of particular interest because such processes could be used to design novel catalytic transformations based on bimetallic cooperation.[4] Compounds in which two metals are held in close proximity by a labile d^8–d^{10} bond[5] are likely intermediates for these reactions. Indeed, silver(I) has been shown to catalyze methyl scrambling on the compound [(bpy)PtMe$_2$] (bpy = 2,2′-bipyridyl), and this process is thought to involve the sandwich complex {[(bpy)PtMe$_2$]$_2$Ag}$^+$, which contains two dative Pt^{II}→Ag^{I} bonds.[5a] We recently reported the synthesis of related adducts of the complex [(NN)PtMe$_2$] (NN = 2,3-bis(2,6-dichlorophenyl)iminobutane) with copper(I).[6] However, these compounds do not undergo transmetalation; much to our disappointment, their reactivity in solution is dominated by platinum-to-copper electron transfer, whereas, in the gas phase, dissociation of the α-diimine ligand is observed. We now present a mass-spectrometric study of a series of related systems with 1) stabilizing phosphines bound to copper and 2) the stronger chelating ligand bis(dimethylphosphino)ethane (dmpe) on platinum. These systems undergo two types of transmetalation in the gas phase, and in one case the activation energies for both processes were measured[7,8] and compared with density functional theory (DFT) calculations. Additionally, we characterized an unexpectedly stable intermediate with a Pt^{II}–Cu^{I} bond and a bridging methyl group by X-ray diffraction (XRD) crystallography.

The bimetallic cations **4a–d** were electrosprayed on a Thermo-Finnigan TSQ Quantum instrument from solutions containing equimolar amounts of [(dmpe)PtMe$_2$][9] (**1**), copper(I) triflate (**2**), and a monodentate phosphine (**3a–d**, Scheme 1), and were identified by their *m/z* ratio and isotope pattern. To obtain the structural information that is not available from mass spectrometry, the cation **4d** was crystallized as its triflate salt **4d**-OTf by addition of ether to an equimolar solution of **1**, **2**, and **3d** in thf and subsequent cooling to −20 °C (details and characterization in the Supporting Information). XRD analysis[10] of **4d**-OTf and of its platinum precursor **1** (Figure 1) provided information about the binding of the [(R$_3$P)Cu]$^+$ fragment to **1**. The Cu^{I} atom in **4d**-OTf has short contacts to both the Pt^{II} center (2.5275 Å) and one methyl carbon atom (2.090 Å). The latter contact is only slightly longer than the Cu–C bonds in reported methylcopper(I) complexes[11] (between 1.916 Å in [(1,3-bis(2,6-diisopropylphenyl)imidazolyliden)CuMe][11a] and 2.042 Å in [(Ph$_3$P)$_3$CuMe][11b]). Furthermore, the copper-



Scheme 1. Generation of ions **2a–d**.

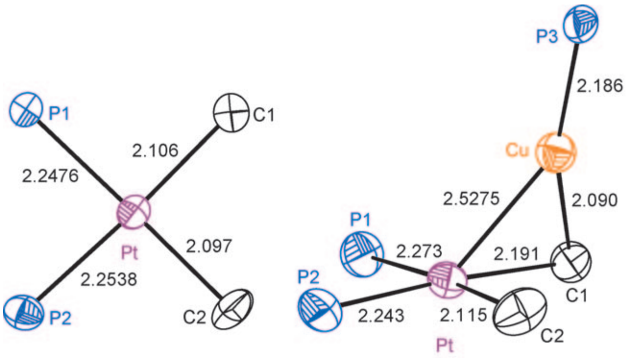


Figure 1. Thermal ellipsoid (50% probability) representations of the first coordination sphere of the metal centers in compounds **1** and **4d**-OTf and selected bond lengths [Å]. For clarity, hydrogen atoms are omitted and only the main position (94% occupancy) of the Cu atom in **4d**-OTf is plotted.

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coordinated Pt–C bond (2.191 Å) is markedly elongated with respect to the other one in **4d**-OTf (2.115 Å) and to those in **1** (2.097 and 2.106 Å). Thus, the methyl group in **4d**-OTf—and consequently in cations **4a–d**—should be seen as bridging between the two metal centers, indicating that transmetalation has already partly taken place in these bimetallic adducts. Several examples of structurally characterized compounds involving bridging methyl groups are known in late-transition-metal chemistry.[12] However **4d**-OTf is, to our knowledge, the first one in which one methyl group is the only bridge, and that makes it a unique intermediate for intermolecular transmetalation.

With this structural information in hand, we turn to the gas-phase reactivity of cations **4a–d**. Upon collision-induced dissociation (CID) with argon (0.2 mTorr) at a collision offset of 50 V, **4a** undergoes two distinct reactions involving the formation of a Cu–Me bond (Figure 2). In the first one (Scheme 2a), a neutral methylcopper(I) (**6**) molecule[13] is eliminated with concomitant migration of the PMe_3 ligand to the platinum(II) center, forming cation **5a**.[14] In the second reaction (Scheme 2b), PMe_3 stays coordinated to copper(I) while a methyl group is transferred from platinum(II) to copper(I), yielding cation **7** and $[(Me_3P)CuMe]$ (**8a**).[15]

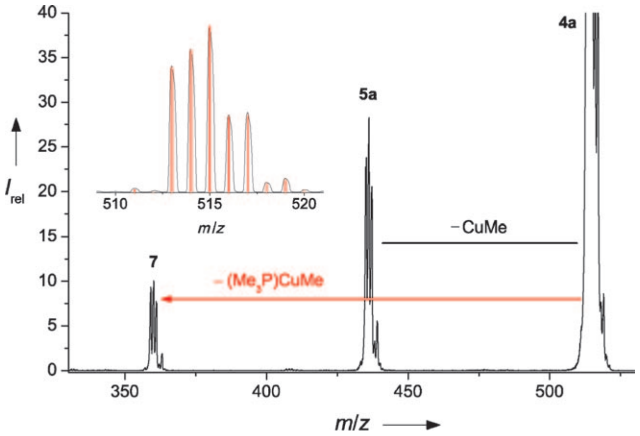
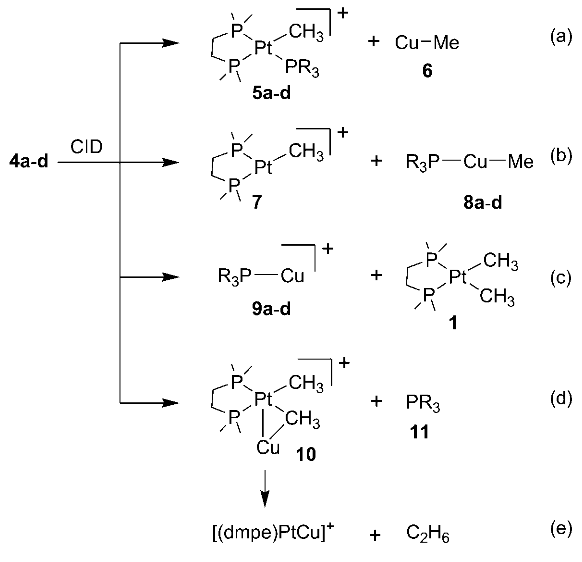


Figure 2. CID spectrum of cation **4a** (0.2 mTorr Ar, 50 V offset). Inset: Experimental (black) and calculated (red) isotope pattern of ion **4a.**



Scheme 2. Observed CID reactions of ions **4a–d**.

For comparison, we investigated the CID reactions of the analogues **4b–d** (Scheme 1), which contain increasingly bulky stabilizing phosphines, under the same conditions. These ions undergo transmetalation reactions analogous to those of **4a**, but two additional fragmentation channels appear, namely rupture of the Pt–Cu or P–Cu bonds (Scheme 2c,d). Additionally, a weak signal corresponding to $[(dmpe)PtCu]^+$ was observed, which we attribute to ethane loss from $\{(dmpe)PtMe_2]Cu\}^+$ (**10**, Scheme 2e). Branching ratios (Table 1) for these reactions were obtained by integration of the corresponding peaks in the CID spectra. These data show that reaction (a) is hampered by bulky phosphines and is completely absent for $(tBu)_3P$, presumably because of the destabilization of the cationic product **5d**—and the transition state leading to it—by steric repulsion between the methyl groups of the dmpe and $(tBu)_3P$ ligands. Reaction (b) is available to all four ions and becomes predominant for **4c** and **4d**, for which the rupture of the Pt–Cu bond is also competitive. The low overall yield for the fragmentation of these two ions indicates their increased stability. In contrast, the PPh_3 ligand in ion **4b** appears not to be bulky enough to significantly slow down reaction (a) with respect to reaction (b), but being a weaker σ-donor ligand than trialkylphosphines, it allows reaction (d) to become kinetically competitive.

Table 1: Branching ratios[a] of the fragmentation products (Scheme 1) and total conversion yield of **4a–d** collided with 0.2 mTorr Ar at 50 V offset.

Ion	(a)	(b)	(c)	(d)	(e)	Residual[b]	Conv. [%]
4a	0.73	0.24	–	–	–	0.03	21.0
4b[c]	0.78	0.13	–	0.05	0.02	0.01	13.7
4c	0.10	0.49	0.30	0.02	0.01	0.08	1.5
4d	–	0.67	0.15	0.02	0.02	0.14[d]	3.4

[a] Defined as $I_i/(I_{tot}-I_R)$, where I_i and I_R are the integrated intensities of the product i and the reactant ion, respectively, and I_{tot} is the total ion intensity. [b] Defined as the integration of the full mass range outside the peak regions divided by I_{tot}. [c] Measured on a single mass-selected isotopic signal because of partial overlap of the isotope pattern of **4b** with a weak, unidentified signal. [d] Weak signals corresponding to loss of *tert*-butyl radical or isoprene from the ions containing $(tBu)_3P$ are observed.

Thermochemical information for the transmetalation reactions of **4a** was obtained by recording energy-resolved reactive cross-section data (Figure 3) as previously described[8h] (see the Supporting Information), from which activation energies were extracted using our program L-CID.[16] For an accurate treatment of the kinetic shift, one needs to distinguish between so-called tight and loose transition states.[16] The former is a regular transition state connecting two energy minima on the potential-energy surface of the reaction, whereas the latter arises from the centrifugal barrier

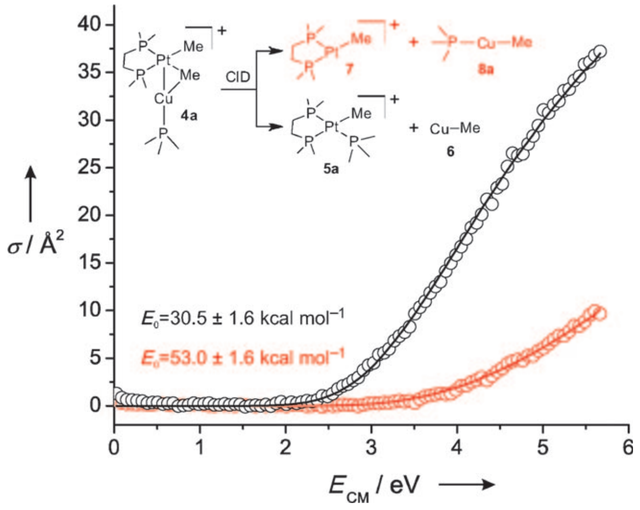


Figure 3. Zero-pressure extrapolated cross-sections (circles) and L-CID fitted curves (lines) as a function of center-of-mass energy for the two competing CID reactions of ion **4a**.

for a dissociation reaction that has no electronic reverse activation barrier. According to DFT calculations (see below), the products of reaction (b) lie approximately 24 kcal mol^{-1} above those of reaction (a). Since both channels are observed, this large difference in reaction enthalpy has to be compensated by a more favorable entropy of activation for reaction (b). Consequently, we infer that the rate-limiting transition state is tight for reaction (a) and loose for reaction (b). Using these arguments, we obtained activation energies of 30.5 ± 1.6 and 53.0 ± 1.6 kcal mol^{-1} for reactions (a) and (b), respectively. It is worth noting that the reactions observed in the gas phase involve undercoordinated species that would be additionally stabilized in solution; thus, solvent effects are likely to lower the corresponding barriers in the condensed phase.

A more detailed mechanistic picture of the fragmentation reactions of **4a** was obtained by means of DFT calculations (Figure 4). Geometries[17] were optimized using the Gaussian 03 program suite[18] at the BP86/6-31G(d,p) level, which was shown to reproduce the experimental structures of **1**, **4d**, and **6** accurately (see the Supporting Information). Energies were computed using the ADF suite,[19] initially at the BP86/TZP level, but this method predicts the final dissociation—which corresponds to a loose transition state—to be rate-limiting for both reactions (a) and (b), which is inconsistent with experimental data. Thus, energies were evaluated using the MPW1K functional,[20,21] which was designed for accurate kinetic predictions and was successfully applied to related gas-phase Pt^{II} chemistry.[22] This computational investigation shows that, in reaction (a), the Cu atom migrates from one side of the coordination plane of the Pt^{II} center to the other via a rate-limiting transition state **TS1** in which the P–Pt bond is partially formed. The resulting complex **11** then eliminates methylcopper(I) (**6**) to yield the observed ion **5a**. Reaction (b) proceeds via a methyl-bridged intermediate **12**, in which the Pt, C, and Cu atoms are in a quasi-linear arrangement. The rate-limiting dissociation of the transmetalation product **8a** exhibits no reverse activation barrier. Reaction (c) starts

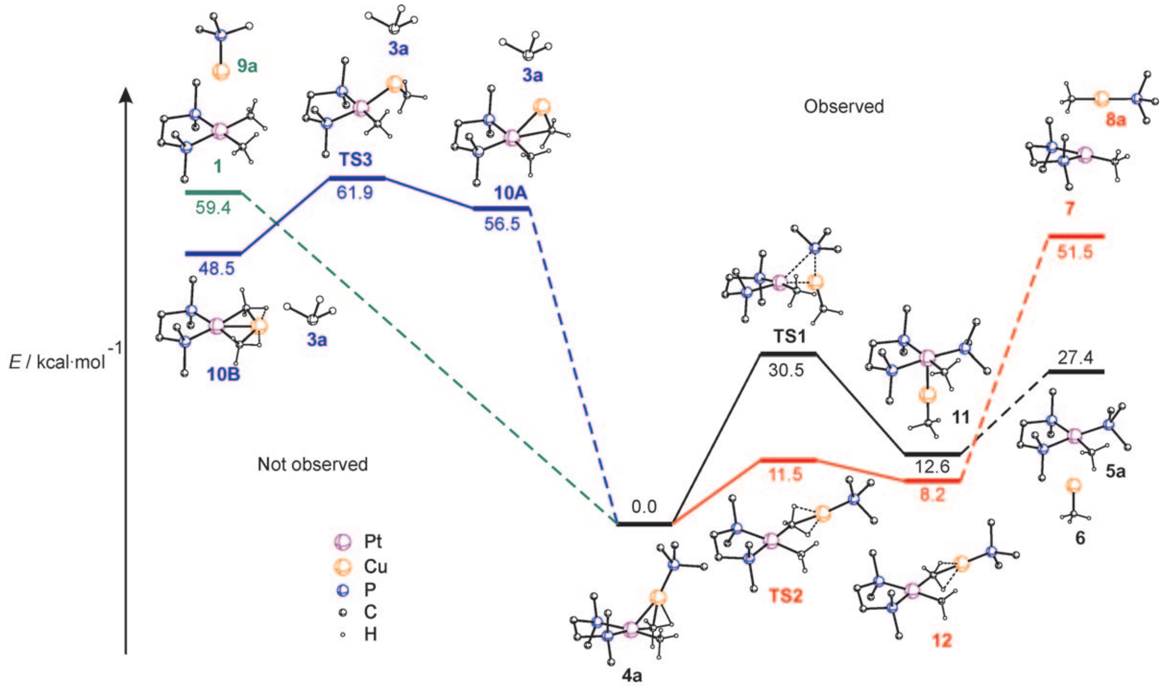


Figure 4. Calculated (MPW1K/TZP//BP86/6-31G(d,p);Pt,Cu:SDD) potential-energy surface for the observed (right: (a) black, (b) red) and absent (left: (c) blue, (d) green) dissociation channels of **4a**. Dashed lines indicate dissociations that proceed without a reverse activation barrier. For clarity, all hydrogen atoms except those of the metal-bound methyl groups are excluded. Complete structural and energetic details are in the Supporting Information.

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with dissociation of PMe_3 to form **10A**, which then rearranges via **TS3** to the more stable planar isomer **10B**. No intermediate was found for reaction (d). The computed energies are in good agreement with the experimental results for the two observed reaction channels (a: 30.5 vs. 30.5; b: 51.5 vs. 53.0 $kcal\,mol^{-1}$), and the two absent ones are predicted to be more endothermic (Figure 4). The good performance of the MPW1K functional for this challenging system containing metal–metal bonds is promising, but it is unclear at this stage whether this method is more generally applicable. Future studies will hopefully provide a larger set of experimental energies that will allow a thorough examination of the performance of DFT methods for related systems.

In summary, platinum-to-copper methyl transfer has been demonstrated in the gas phase. Activation energies have been measured for two distinct transmetalation pathways, and are well reproduced by DFT calculations using Truhlar's MPW1K functional. Additionally, we isolated and structurally characterized a novel bimetallic intermediate in which the two metals are connected only by a short bond and a single bridging methyl group. An interesting feature of the system described herein is its high modularity: variation of the coinage metal, the phosphine ligands, and the hydrocarbyl groups will be used in future work to hopefully provide detailed insight in the factors controlling transmetalation.

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[15] Cation **7** could in principle also be formed by dissociation of PMe_3 from **5a**. The products of such a sequential process would be higher in energy than those of reaction (b) by an amount corresponding to the binding energy of PMe_3 to the CuMe moiety. Thus, this process is unlikely to play a significant role in the observed fragmentation and was not included in the modeling.

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