Chemoselective NHC Transmetallation

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Relative Lability and Chemoselective Transmetallation of NHC in Hybrid Phosphine-NHC Ligands: Access to Heterometallic Complexes

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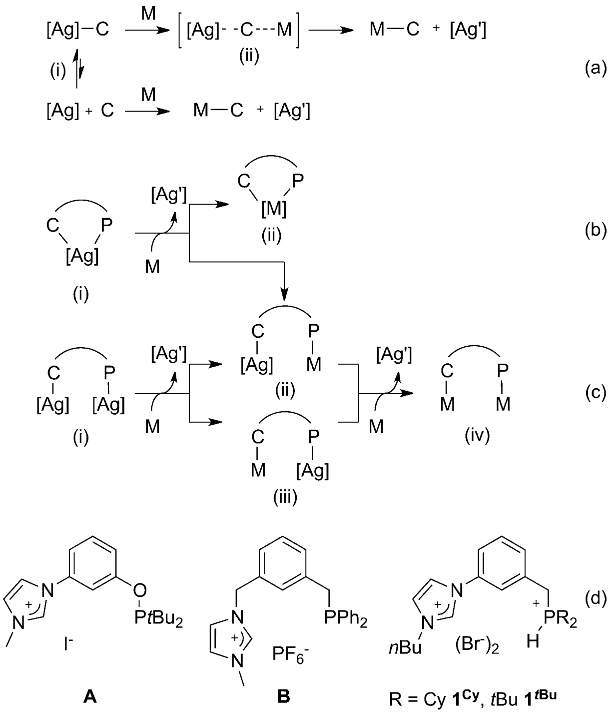
Abstract: *The relative lability and transmetallation aptitude of trialkylphosphine and NHC donors, integrated in semi-rigid hybrid ligands attached to [Ag$_4$Br$_4$] pseudo-cubanes, lies in favor of the NHC and is used to selectively access unprecedented NHC complexes with heterobimetallic cores, such as Ag–Cu (**4**^{Cy}) and Ag–Ir (**5**^{tBu}). These can be viewed as an arrested state before the full transmetallation of both donors, which gives the homodinuclear Cu (**3**^{Cy}) and Ir (**6**^{Cy}) complexes. The observed NHC transmetallation aptitude and reactivity urges caution in the common notion that views the NHC as a universal spectator.*

The bonding analogy between phosphines and N-heterocyclic carbenes (NHCs), and the stronger σ-donor ability of the latter, implies that NHC ligands are less prone to substitution than PR$_3$ under comparable molecular environments (that is, nature of metal, co-ligands, and coordination geometry).[1] Current computational and experimental methods provide a solid understanding of metal–NHC bonding across the periodic table.[2] In late transition metals, and in contrast to M-PR$_3$, strong and irreversible M–NHC binding dictates the nature of the complexes formed.[3] In numerous cases, phosphine substitution by NHCs has been used for the synthesis of NHC-complexes (for example, Ru,[4] Fe,[5] Ni,[6] Pd,[7] and Pt[8]). In contrast, the substitution of coordinated NHCs by phosphines is scarce.[9]

Within the group 11 metals, the M−NHC bond strength follows the order Au^{I} > Cu^{I} > Ag^{I},[1a,10] which underlies the widespread application of Ag–NHC complexes as reagents for the synthesis of diverse transition metal–NHC complexes by transmetallation. The detailed mechanisms of transmetallation remain vague:[11] plausible propositions include the involvement of free NHCs formed in situ after the establishment of equilibria on dissolution of the Ag–NHC species, or the presence of transient (hetero)di- or poly-nuclear intermediates with bridging NHC ligands (Scheme 1 a),[12] by analogy with the now recognized bridging aptitude of phosphines.[13] Recent cases of apparently transmetallation-inert species,[14] anomalous "reverse transmetallations" to Ag,[15] and facile NHC dissociation from heavier transition metals are relevant and perplexing.[16] Understanding the elementary steps of transmetallation and the associated driving forces constitute important research targets with implications in homogeneous catalysis, supramolecular self-assembly, and materials synthesis.



Scheme 1. a) Plausible mechanisms for the transmetallation from Ag–NHC complexes involving dissociation of the NHC or formation of bridging NHC intermediates; b) chelating or c) bridging coordination modes of hybrid P-NHC with Ag and their transmetallation; d) hybrid P–NHC pro-ligands, previously reported by our group (**A** and **B**),[14a] and studied in this work (**1**^{Cy} and **1**^{tBu}).

Hybrid ligands comprising NHC and phosphine donors are of considerable interest for the study of selective metal–ligand interactions.[17] Whereas Ir pincer complexes are directly accessible from **A** (Scheme 1 d),[14a] but not by transmetallation from the corresponding Ag complex, suggesting that the pathways shown in Scheme 1 b,c were not operative, transmetallations of other P-NHC hybrid ligands from Ag to Ru,[18] Pd[14b,19] and Rh[20] have been reported.

To gain insight into this unexpected behavior, we targeted the new ligands **1**^{Cy} and **1**^{tBu}, containing alkyl-phosphine donors (electronically more similar to NHC) (Scheme 1 d). In principle, they can adopt chelating (b(i)) or bridging (c(i))

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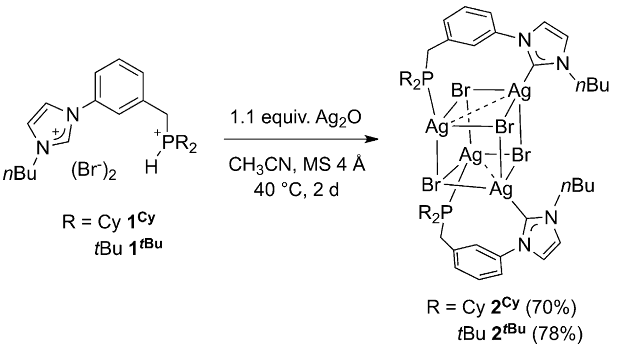
coordination modes, display hemilability and, on transmetallation, can lead to the b(ii) and c(iv) species, respectively. We provide here evidence that heterometallic intermediates, such as c(ii) and c(iii) involving bridging P–NHC ligands, can indeed be detected, and we shed light on important transmetallation chemoselectivity issues.

Reactions of $\mathbf{1}^{\mathbf{Cy}}$ or $\mathbf{1}^{\boldsymbol{t}\mathbf{Bu}}$ (Supporting Information) with Ag_2O (Scheme 2) gave good yields of $\mathbf{2}^{\mathbf{Cy}}$ and $\mathbf{2}^{\boldsymbol{t}\mathbf{Bu}}$, respectively, which in the solid state feature a distorted pseudo-cubane $[Ag_4Br_4]$ core with bridging hybrid ligands between P-coordinated (Ag^P) and NHC-coordinated (Ag^C) Ag centers (Figure 1). This arrangement results in chiral molecular structures and both enantiomers are present in the unit cell.



Scheme 2. Synthesis of pseudo-cubane complexes $\mathbf{2}^{\mathbf{Cy}}$ and $\mathbf{2}^{\boldsymbol{t}\mathbf{Bu}}$. Yields are based on the ligand.

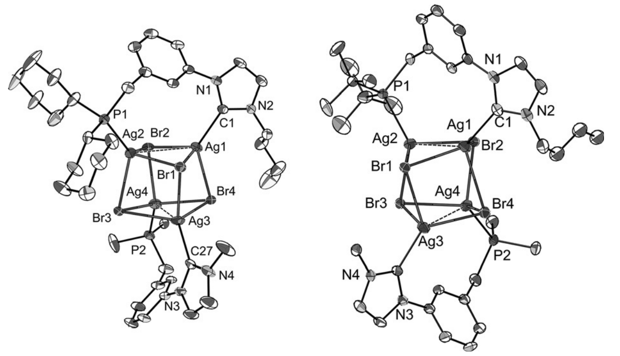
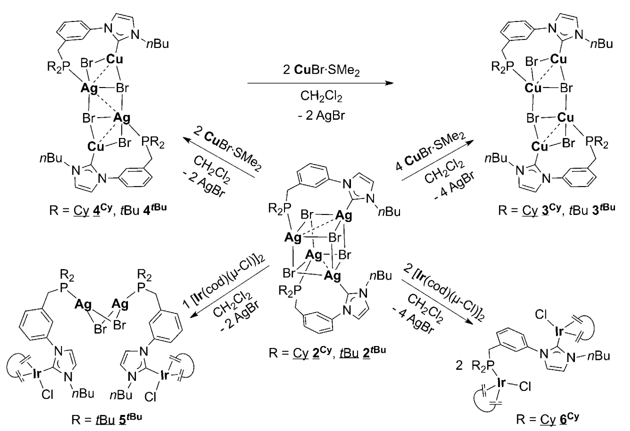


Figure 1. Molecular structures of $\mathbf{2}^{\mathbf{Cy}}$ (left) and $\mathbf{2}^{\boldsymbol{t}\mathbf{Bu}}$ (right) (thermal ellipsoids at 30% probability). For clarity, Cy, *t*Bu, and *n*Bu groups are only shown in the ligands at the top. Only one disordered position for the Cy group in $\mathbf{2}^{\mathbf{Cy}}$ and the *n*Bu group in $\mathbf{2}^{\boldsymbol{t}\mathbf{Bu}}$ is displayed. H atoms and crystallization solvent are omitted. Metrical data are given in the Supporting Information.[30]

While the $[Ag_4(halide)_4(phosphine)_4]$ motif (phosphine = monodentate tertiary phosphine) is ubiquitous, it is noteworthy that $[Ag_4(halide)_4(carbene)_4]$ (carbene = monodentate NHC) is unknown. However, $[Ag_4(halide)_4L_2]$ (L = rigid methylene- or 1,3-phenylene-bridged bis-NHCs),[21] and $[Ag_4I_4(P\text{-}NHC)_2]$ have recently been described.[14,22]

Evidence from DOSY NMR spectroscopy supported the idea that the cubane integrity of $\mathbf{2}^{\mathbf{Cy}}$ and $\mathbf{2}^{\boldsymbol{t}\mathbf{Bu}}$ was maintained in solution. While $\mathbf{2}^{\boldsymbol{t}\mathbf{Bu}}$ was rigid at room temperature, a fluxional process was observed for $\mathbf{2}^{\mathbf{Cy}}$, where two ^{31}P NMR doublets, well resolved below −8 °C, coalesced at ambient temperature (Supporting Information). A $\Delta G^{\ddagger}$ of $57\pm2\,\mathrm{kJ\,mol^{-1}}$ was calculated for this process from variable temperature measurements. Furthermore, the ^{13}C NMR singlets for the C_{NHC} resonances of $\mathbf{2}^{\mathbf{Cy}}$ and $\mathbf{2}^{\boldsymbol{t}\mathbf{Bu}}$ were rationalized by the fast exchange between the NHC donor arms.[21b,23] The reaction of $\mathbf{2}^{\boldsymbol{t}\mathbf{Bu}}$ with S_8 resulted in instantaneous $P{=}S$ formation and concomittant AgBr precipitation, again consistent with P fluxionality. Consequently, we propose that two separate exchange processes may be taking place (involving the pairs of Ag^P and Ag^C), but under the conditions used, no cross-exchange between Ag^P and Ag^C was observed (see the Supporting Information, Section I.5.3). Thus, in the present system, although donor group lability as inferred by the dynamic behavior of the cubanes in solution appears to be a prerequisite for the kinetically controlled ligand transfer to another metal, it is not always sufficient. This is also demonstrated by the lack of ligand scrambling between $\mathbf{2}^{\mathbf{Cy}}$ and $\mathbf{2}^{\boldsymbol{t}\mathbf{Bu}}$, which is attributable to kinetic reasons.

To correlate the above mentioned dynamic processes with reactivity, the ligand transmetallation from the cubanes to Cu and Ir centers was investigated (Scheme 3).



Scheme 3. Transmetallation from cubanes (**2**) to the heterometallic Ag-Cu (**4**) and Ag-Ir (**5**), and the homodinuclear Cu (**3**) and Ir (**6**) complexes. Compounds underlined have been structurally characterized.

In the rare past cases where hybrid NHC ligands have been used in transmetallation from Ag to Cu, concomitant transfer of both donor groups was facile and kinetically indistinguishable.[12c,24] Accordingly, the reactions of $\mathbf{2}^{\mathbf{Cy}}$ and $\mathbf{2}^{\boldsymbol{t}\mathbf{Bu}}$ with 4 equiv $CuBr{\cdot}SMe_2$ (Ag/Cu = 1:1) in CH_2Cl_2 resulted in the complete exchange of Ag by Cu and the isolation of the ladder-type tetranuclear species $\mathbf{3}^{\mathbf{Cy}}$ and $\mathbf{3}^{\boldsymbol{t}\mathbf{Bu}}$ (Figure 2). The same complexes were also obtained from $\mathbf{1}^{\mathbf{Cy}}$ and $\mathbf{1}^{\boldsymbol{t}\mathbf{Bu}}$ and $[Cu(mes)]_5$ (Supporting Information).

In contrast, the use of a Ag/Cu = 2:1 stoichiometry (Scheme 3) led to the heterotetranuclear complexes $\mathbf{4}^{\mathbf{Cy}}$ and $\mathbf{4}^{\boldsymbol{t}\mathbf{Bu}}$, in which transfer from Ag to Cu of only the NHC donor took place, while the phosphine donor remained attached to Ag (Figure 3).

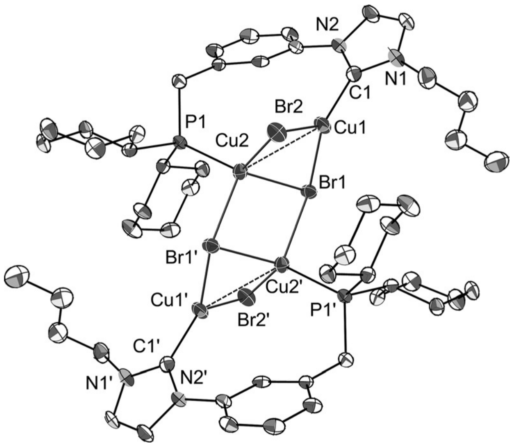


Figure 2. Molecular structure of the centrosymmetric **3**^{Cy} (thermal ellipsoids at 40% probability). Hydrogen atoms are omitted. See the Supporting Information for metrical data.[30]

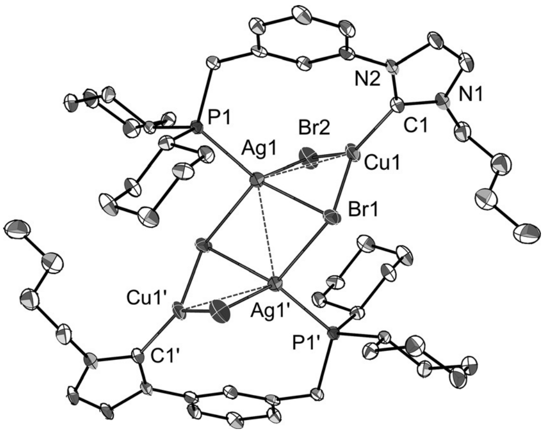


Figure 3. Molecular structure of the centrosymmetric **4**^{Cy} (thermal ellipsoids at 40% probability). Hydrogen atoms are omitted. See the Supporting Information for metrical data.[30]

Monitoring the transmetallation of **2**$^{t\mathrm{Bu}}$ with excess CuBr·SMe$_2$ (>4 equiv) by NMR spectroscopy at low temperatures confirmed that the more labile (but stronger σ-donating) NHC donor transmetallated faster, since **4**$^{t\mathrm{Bu}}$ appeared to be the only detectable intermediate on the way to the formation of **3**$^{t\mathrm{Bu}}$ (Supporting Information, Section I.8). Remarkably, the P–Ag couplings were retained during the NHC transmetallation, pointing to the absence of Cu/Ag exchange on the P site and showing that the opposite heteronuclear complex (P–Cu, NHC–Ag) is not formed as an intermediate. The structure of **4**^{Cy}, which appears to be the first for a mixed Cu/Ag/NHC complex (CCDC), is similar to that of **3**^{Cy}, but displays Ag^{I}···Ag^{I} (3.006(1) Å) and Cu^{I}···Ag^{I} metallophilic interactions (2.838(1) Å).[25]

Further insight into the transmetallation reactivity was provided when **2**$^{t\mathrm{Bu}}$ was reacted with 1 equiv [Ir(cod)(μ-Cl)]$_2$ (Ag/Ir = 2:1 stoichiometry) for 2 h at room temperature, leading to the isolation of the new heterotetranuclear Ag–Ir complex **5**$^{t\mathrm{Bu}}$ (Scheme 3). Two characteristic doublets in the ^{31}P{^{1}H} NMR spectrum confirm the P–Ag coordination. The structure of **5**$^{t\mathrm{Bu}}$ established the transfer of the NHC donor from Ag to Ir, while the phosphine group remained attached to Ag (Figure 4). The two Ag(μ-P-NHC)Ir moieties are connected by bromide bridges and weak argentophilic interactions.[25,26] This structure appears to be the first for a molecular Ir/Ag/NHC complex (CCDC).

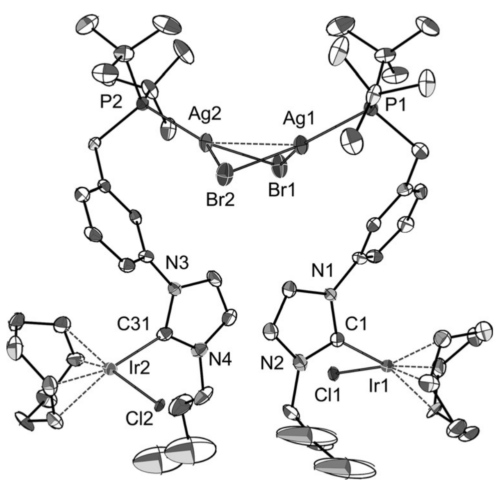


Figure 4. Molecular structure of **5**$^{t\mathrm{Bu}}$ (thermal ellipsoids at 40% probability). Hydrogen atoms are omitted. See the Supporting Information for metrical data.[30]

Interestingly, the corresponding heterometallic complex could not be accessed from the reaction with the cyclohexyl analogue **2**^{Cy}, but instead, the diiridium complex **6**^{Cy} (Figure 5) was isolated in low yields. The latter was obtained more efficiently when 2 equiv of [Ir(cod)(μ-Cl)]$_2$ (Ag/Ir = 1:1 stoichiometry) were used.

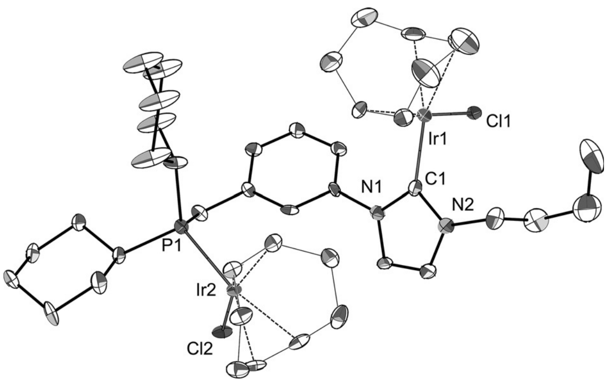


Figure 5. Molecular structure of **6**^{Cy} (thermal ellipsoids at 35% probability). Hydrogen atoms are omitted. See the Supporting Information for metrical data.[30]

A related bridging P–NHC ligand in a diiridium complex has been recently reported.[14a] Rationalization of the formation of **5**$^{t\mathrm{Bu}}$ and **6**^{Cy} may invoke additional differences in the lability of the P arm of the ligand, owing to the different phosphine substituents. Indeed, transfer and strong coordination of a functionalized di-*tert*-butyl phosphine to silver[27] could explain the isolation of the heterobimetallic Ag–Ir complex $\mathbf{5}^{t\mathrm{Bu}}$. In the cyclohexyl case, competition between phosphine and NHC substitution may be due to a weaker P–Ag bond (although the Tolman electronic parameters (TEP) of PCy_3 and $P(tBu)_3$, 2056.4 cm^{-1} and 2056.1 cm^{-1}, respectively, are very similar),[28] leading only to the isolation of the homometallic Ir complex $\mathbf{6}^{\mathrm{Cy}}$, regardless of the amount of iridium precursor used.

In summary, the use of tuneable ditopic P-NHC ligands (P = alkyl phosphine) revealed a subtle balance between the lability of the NHC and the trialkylphosphine donor arms with regard to Ag^I. Differences in the transmetallation aptitude were also established, providing selective synthetic routes for heterometallic species with diverse potential, and shedding light on possible in situ transmetallations that may occur when using mixed-metal systems in catalysis.[29] Surprisingly, in all cases reported here, the NHC transmetallation aptitude is superior to that of the trialkylphosphine.

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Keywords: chemoselectivity · hybrid ligands · N-heterocyclic carbene · phosphines · transmetallation

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[30] CCDC 1409335-1409340 contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

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