Generalization of the Copper to Late Transition Metal Transmetallation to Carbenes beyond N-Heterocyclic Carbenes

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Abstract: *C*arbene transition metal complexes have become a prevalent family of catalysts enabling numerous organic transformations. Their facile synthetic access is a matter of great importance. To this end, the Cu^{I}-NHC transfer methodology has emerged as a powerful alternative presenting attractive advantages over other methods. Herein we report the remarkable ability of copper to not only transfer NHCs but also other types of carbene such as abnormal NHCs (*a*NHCs), cyclic (alkyl)(amino)carbenes (CAACs) and mesoionic carbenes (MICs) to various transition metal precursors.

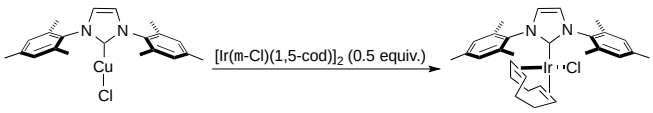
Introduction

In less than three decades, *N*-heterocyclic carbene transition metal complexes (NHC-TM) have led to numerous breakthroughs in catalysis, and have found many other applications.[1-3] The development of catalysts and their usefulness is frequently linked to the simplicity and cost of their synthesis as much as their catalytic efficiency. In this regard, finding new straightforward and economically advantageous synthetic methods to generate NHC-TM complexes is an area of significant interest. The preparation of such complexes (pre-catalysts) is usually accomplished by generating a highly reactive and air- and moisture-sensitive free carbene species, which is subsequently bound to a metal center. The seminal discovery by Lin and co-workers on the ability of Ag^{I}-NHC complexes to transfer Ag-bound NHC ligands to another metal center has led to a dramatic extension of the library of NHC-TM complexes available.[4] Since this report, several methodologies using various metals have been employed to provide alternatives to address the cost and sensitivity of the Ag transmetallation route. The transfer from W^0, reported concomitantly with the silver approach, suffers from a narrow scope and undesirable transfer of carbonyl ligand as a competing reaction.[5] The same drawbacks affect the transfer from other Group VI metals.[5b,6] Transfer from Au^{I}, an expensive metal, requires the presence of PPh_3 to proceed to completion.[7] Only few examples of direct metalation of imidazolium using NiCl^{II}, $Ni(cod)_2$ and Raney Nickel have been reported.[8] It appeared to us that Cu^{I}-NHC transfer could emerge as a more expedient route to NHC-TM complexes.[9] Indeed Cu^{I}-NHC complexes have several advantages over their silver congeners, as most of them are air-, moisture- and light-stable and less prone to undesirable ligand exchanges.[10] However, so far, this methodology has only been applied to the synthesis of ruthenium, rhodium, palladium and gold NHC complexes. Herein we report an extension of the copper transmetallation reaction to iridium NHC complexes. More importantly, we expand this methodology to carbenes beyond classical NHCs,[11] namely mesoionic carbenes (MICs),[12] abnormal NHCs (*a*NHCs),[13] and cyclic (alkyl)(amino)carbenes (CAACs).[14] It must be noted that MIC-, *a*NHCs-, and CAAC-ligated transition metals complexes have already been shown to exhibit high activity in various catalytic applications.[11,15]

Results and Discussion

First, we investigated the possibility of extending the scope of metal acceptors for the Cu^{I}-NHC transfer using an unsaturated NHC, namely IMes (*N*,*N*'-bis-[2,4,6-(trimethyl)phenyl]imidazol-2-ylidene). Considering the importance of NHCs in iridium and rhodium chemistry, both as catalysts and as tools to assess ligand electronic properties using the Tolman Electronic Parameter (TEP),[16] the NHC-Cu^{I} transfer to Ir^{I} and Rh^{I} was examined. Preliminary experiments were conducted with [Cu(Cl)(IMes)] **1** in the presence of $[Ir(\mu\text{-Cl})(1,5\text{-cod})]_2$ (cod = cyclooctadiene) in various solvents and under a number of reaction conditions (Table 1).

Table 1. Optimization of IMes transfer from Cu to Ir.[a]



1 **2**

Entry	Solvent	Temperature	Time	Conversion (%)[b]
1	CH_2Cl_2	rt	1 min	65
2	CH_2Cl_2	40 °C	16 h	66
3	CH_2Cl_2	40 °C	24 h	66
4	pyridine	110 °C	16 h	40
5	MeCN	80 °C	16 h	90
6	**iPrOH**	**80 °C**	**16 h**	**>99 (93)**

[a] Reaction conditions: [Cu(Cl)(IMes)] **1** (0.02 mmol), $[Ir(\mu\text{-Cl})(1,5\text{-cod})]_2$ (0.01 mmol), solvent (1 mL). [b] Conversion determined by ^{1}H NMR based on **1**;

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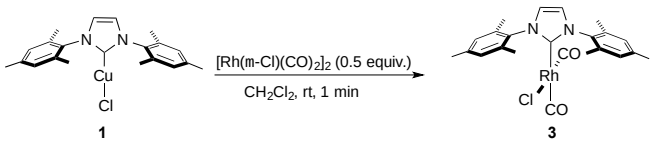
Isolated yield in parentheses.

Interestingly, in dichloromethane, the reaction proceeded instantaneously at room temperature (Table 1, entry 1). The transformation could be observed visually with the formation of insoluble CuCl in the reaction medium after a few seconds. However, the reaction stopped at 65% conversion and neither increasing the temperature to 40 °C or the reaction time (up to 24 hours) led to higher conversion (Table 1, entries 2 and 3). Solvent screening at higher temperatures was carried out. Only moderate conversion (40%) was observed in pyridine at 110°C indicating that the temperature is not the key factor to form [Ir(Cl)(1,5-cod)(IMes)] **2** (Table 1, entry 4). However, the reaction proceeds in higher yields in acetonitrile at 80 °C for 16 hours leading to almost full conversion (90%) (Table 1, entry 5). The transfer of IMes from **1** to **2** finally proceeded to completion in 2-propanol after 16 hours at 80°C, and **2** was isolated in micro-analytically pure form in 93% yield (Table 1, entry 6). To the best of our knowledge, this represents the first example of carbene transfer from copper to iridium.

Similar experiments were conducted using $[Rh(\mu\text{-}Cl)(1,5\text{-}cod)]_2$ but the desired compound [Rh(Cl)(1,5-cod)(IMes)] was never observed as the reaction did not occur or led to decomposition of the starting metallic precursor. However, using $[Rh(\mu\text{-}Cl)(CO)_2]_2$ as a precursor, the reaction proceeded well in dichloromethane at room temperature. Full conversion into NHC-Rh^{I} complex **3** was reached within 1 minute, and **3** was isolated in 89% yield (Scheme 1).

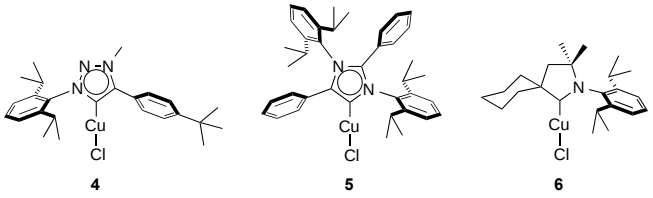


1 3

Scheme 1. IMes transfer from copper complex **1** to rhodium.

So far, only classical saturated and unsaturated NHCs (imidazol-2-ylidenes and imidazolidin-2-ylidenes) as well as cyclopropenylidenes[17] have been successfully transferred from copper to another metal. Having recently reported the preparation of a series of copper complexes supported by mesoionic carbenes (MICs) **4**, abnormal NHCs (*a*NHCs) **5**, and cyclic (alkyl)(amino)carbenes (CAACs) **6** (Figure 1),[18] we investigated the generality of the carbene transfer reaction from copper complexes to other metals.

Treatment of MIC-copper complex **4** with $[Pd(Cl)_2(NCPh)_2]$ afforded the palladium dimer **7** which was isolated in 96% yield after 4 hours at 40 °C in dichloromethane (Fig. 2). Using $[Au(Cl)(SMe_2)]$, as a gold source, the desired MIC-gold complex **8** was obtained in 93% yield after one minute in dichloromethane at room temperature. Similarly, complete formation of the MIC-Ir^{I} complex **9** was observed within one minute at room temperature in CH_2Cl_2. Note that the transmetallation of the MIC ligand to gold and iridium is much easier than those observed with NHCs (Au: 71-90% at 40 °C, 1-2 h;[9b] Ir: 93% at 80 °C, 16 h).



4 5 6

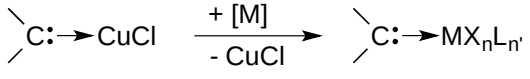
Figure 1. Selected copper complexes for the study of carbene-Cu^{I} transfer reactions.

We propose that these results can be explained by the reduced steric bulk (%V_{Bur}: MIC 33.3; IMes 38.0),[18,19] in spite of the stronger σ-donor properties of MICs compared to NHCs.[15b,16] Finally, just as in the case of NHCs, the [Rh(Cl)(1,5-cod)(MIC)] could not be prepared but the corresponding carbonyl complex **10** was obtained quantitatively.

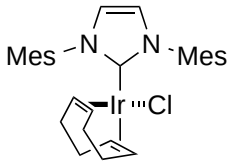
Transfer of the *a*NHC from copper complex **5** occurred in the same manner as for **4** with all metal precursors. Pd^{II}-*a*NHC dimer **11** was obtained in 92% yield after 4 hours at 40°C in CH_2Cl_2, while the Au^{I}-, Ir^{I}- and Rh^{I}-*a*NHC complexes **12**-**14** were isolated in 96%, 80% and 80% yield, respectively, after just one-minute reaction time at room temperature in dichloromethane.

Similar reaction conditions were employed for the formation of Pd^{II}- and Ir^{I}-CAAC complexes **15** (75%) and **17** (83%) from the Cu^{I}-CAAC complex **6**. The synthesis of the neutral Au^{I}-CAAC complex **16** was more problematic. When the reaction was performed in dichloromethane at room temperature, the expected gold complex **16** was formed along with another complex, which is the homoleptic $[Au(CAAC)_2]^+[X]^-$ species described previously.[20] The transformation of neutral gold complexes of **16** into the corresponding cationic bis-(CAAC) Au^{I} complex has already been observed. However when acetonitrile was used as the solvent, the formation of the homoleptic complex was entirely suppressed, and complex **16** was isolated in 89% yield after 45 minutes at room temperature.

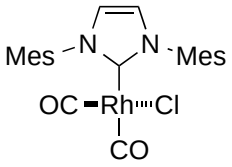
All complexes were fully characterized by standard spectroscopic techniques and structural data were obtained by single crystal X-ray diffraction for **7**-**11**, **13**, **15** and **16** (Fig. 3).[21]



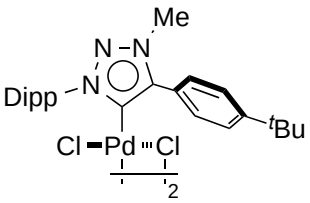
4, **5** and **6** $MX_nL_{n'}$: Pd(μ-Cl)Cl, AuCl, IrCl(1,5-cod), $RhCl(CO)_2$



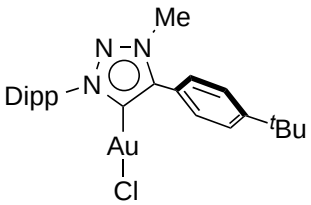
2, 93%[a]



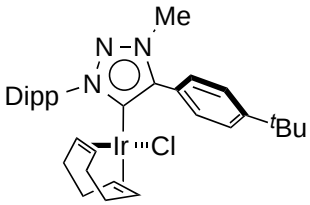
3, 89%[b]



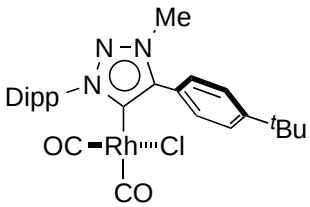
7, 96%[c]



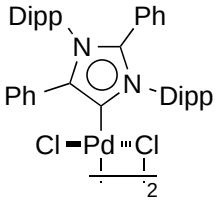
8, 93%[b]



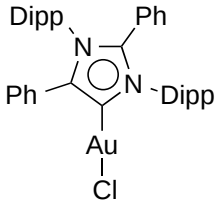
9, 85%[b]



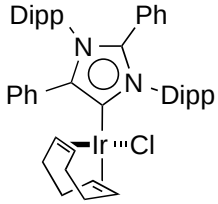
10, 99%[b]



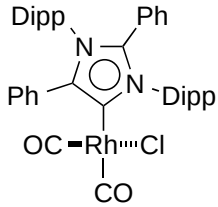
11, 92%[c]



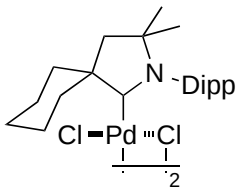
12, 96%[b]



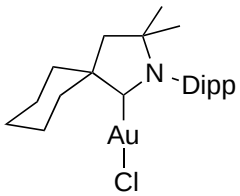
13, 80%[b]



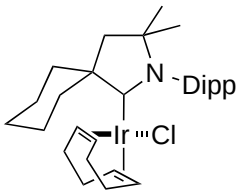
14, 80%[b]



15, 75%[c]



16, 89%[d]



17, 83%[b]

Reaction conditions: [a] *i*PrOH, 80 °C, 16 h; [b] CH_2Cl_2, rt, 1 min; [c] CH_2Cl_2, 40 °C, 4 h; [d] CH_3CN, rt, 45 min.

Figure 2. Carbene transfer from copper to Pd^{II}, Au^{I}, Ir^{I} and Rh^{I}.

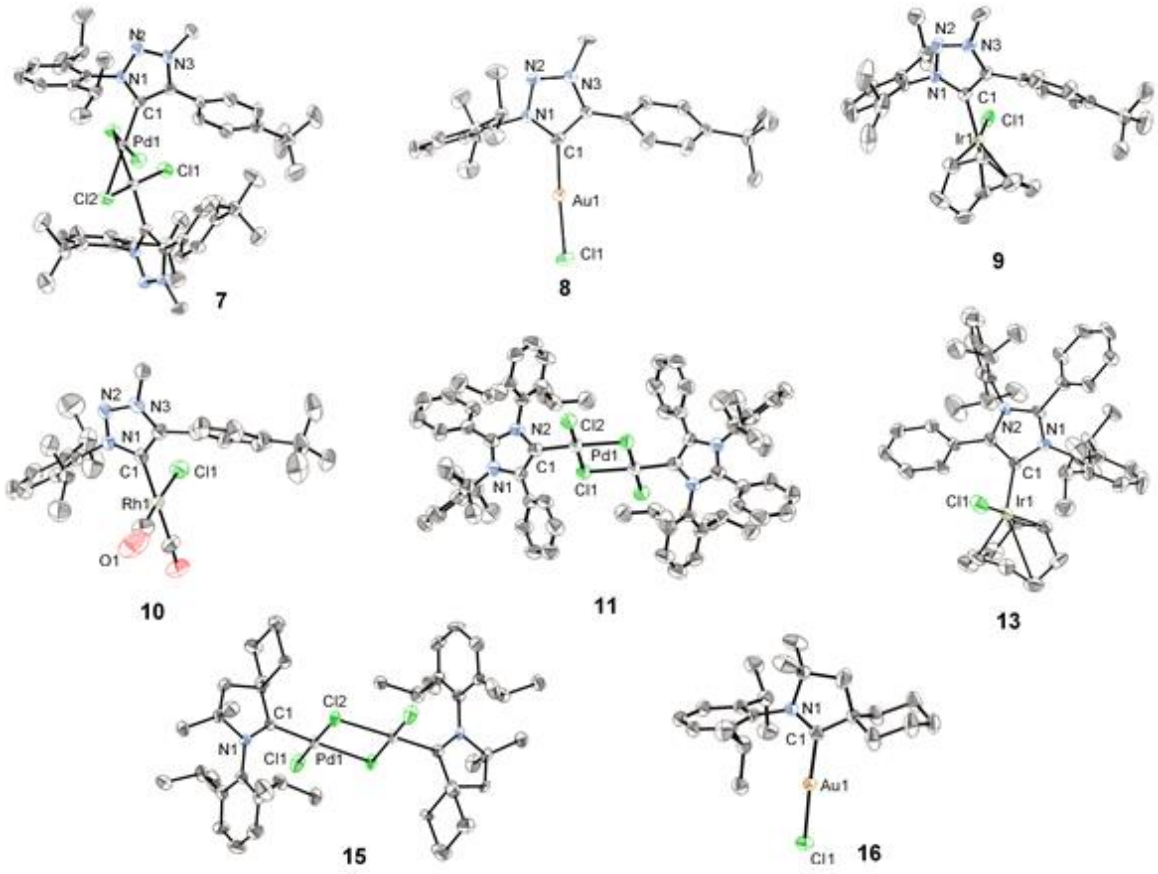
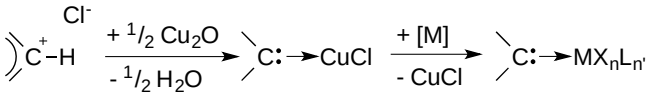


Figure 3. Molecular structures of **7**, **8**, **9**, **10**, **11**, **15** and **16**. Hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (º): **7**: Pd1-C1, 1.951(5); Pd1-Cl1, 2.2823(12); Pd1-Cl2, 2.3316(11); Pd1-Cl2[1], 2.4253(15); **8:** Au1-C1, 1.982(8); Au1-Cl1, 2.276(3); C1-Au1-Cl1, 176.3(3); **9**: Ir1-C1, 2.036(4); Ir1-Cl1, 2.3700(13); C1-Ir1-Cl1, 90.74(13); **10**: Rh1-C1, 2.081(9); Rh1-Cl1, 2.361(3); C1-Rh1-Cl1, 89.6(3); **11**: Pd1-C1, 1.952(8); Pd1-Cl1, 2.289(3); Pd1-Cl2, 2.420(2); Pd1-Cl2[1], 2.343(3); **13**: Ir1-C1, 2.058(9); Ir1-Cl1, 2.338(2); C1-Ir1-Cl1, 89.4(2); **15**: Pd1-C1, 1.937(11); Pd1-Cl1, 2.274(3); Pd1-Cl2, 2.343(3); Pd1-Cl2[1], 2.427(3); **16:** Au1-C1, 1.980(3); Au1-Cl1, 2.2870(8); C1-Au1-Cl1, 176.89(7).[25]

Conclusions

We have successfully synthesized a library of transition metal complexes bearing several different carbenes using Cu^{I} transfer as the synthetic methodology. With the present report, the scope of the NHC-transfer reaction has considerably evolved as it has been extended to Group IX metals and to ligands beyond conventional *N*-heterocyclic carbenes. Of particular interest, the transmetallation occurred under mild conditions, as most reactions can be performed at room temperature and occur within one minute. Since all copper complexes used as precursors can be made by direct metallation of easy to handle carbene conjugate acids with copper oxide, the methodology reported herein allows for the preparation of a variety of carbene complexes without using highly sensitive materials and thus alleviates the need for sophisticated experimental techniques. Therefore, the sequence described in Scheme 2 fulfills the most important criteria for the development of catalysts, i.e. an economical, versatile and simple synthetic access to a library of complexes.



Scheme 2. Straightforward access to a variety of carbene-TM complexes from the carbene conjugate acids via copper-carbene complexes.

Experimental Section

General considerations: All reactions were performed under inert atmosphere using standard Schlenk and glovebox techniques unless otherwise stated. Solvents were dispensed from a solvent purification system. All other reagents were used without further purification. ^{1}H and $^{13}C\{^{1}H\}$ Nuclear Magnetic Resonance (NMR) spectra were recorded on

a Bruker AVANCE 300, a Bruker AVANCE 400 Ultrashield or a Bruker AVANCE 500 spectrometer using the residual solvent peak as reference ($CDCl_3$: δ_H = 7.26 ppm, δ_C = 77.16 ppm; C_6D_6, δ_H = 7.16 ppm, δ_C = 128.06 ppm; CD_3CN, δ_H = 1.94 ppm, δ_C = 1.32 and 118.26 ppm and CD_2Cl_2, δ_H = 5.32 ppm, δ_C = 53.84 ppm) at 298K. IR spectra were recorded on IRAffinity-1 SHIMADZU instrument.

General procedure for Cu^I-carbene transfer: In a glovebox, a vial was charged with the copper complex, one equivalent amount of the desired metal precursor and the appropriate volume of solvent. The reaction mixture was stirred for the time and at the temperature indicated in Table 1 and Scheme 2. After filtration through Celite, the solution was concentrated to 1 mL; then hexane (10 mL) was added and the precipitate was collected by filtration, washed with hexane (3 x 10 mL) and dried *in vacuo*. The solid was dissolved in acetonitrile or benzene (5 mL). The solution was filtered through a frit and evaporated to dryness, leading to microanalytically pure product. Such a procedure can also be carried out using standard Schlenk techniques outside the glovebox.

Dichloro[1-(2,6-diisopropylphenyl)-3-(methyl)-4-(4-tert-butylphenyl)-1,2,3-triazol-5-ylidene]palladium(II) dimer (7): Brownish microcrystalline solid (56 mg, 96%). ^{1}H NMR (500 MHz, CD_2Cl_2, 298K): δ (ppm) = 7.93 (d, ^3J(H,H) = 8.3 Hz, 4H, CH_{Ar}), 7.70-7.65 (m, 6H, CH_{Ar}), 7.42-7.37 (m, 4H, CH_{Ar}), 4.04 (s, 6H, N-CH_3), 2.49-2.40 (m, 4H, CH-CH_3), 1.51-1.40 (m, 18H, CH_3), 1.32-1.15 (m, 12H, CH_3-CH), 1.06-0.89 (m, 12H, CH_3-CH).^{13}C-{^{1}H} NMR (125 MHz, CD_2Cl_2, 298K): δ (ppm) = 153.9 (s, Pd-$C_{triazolylidene}$), 147.1 (s, C^{IV}), 146.7 (s, C^{IV}), 143.6 (s, C^{IV}), 134.9 (br. s, C^{IV}), 131.7 (s, CH_{Ar}), 130.4 (s, CH_{Ar}), 126.4 (s, CH_{Ar}), 124.5 (br. s, CH_{Ar}), 123.4 (s, C^{IV}), 38.5 (s, N-CH_3), 35.3 (s, C^{IV}), 31.4 (s, CH-CH_3), 29.3 (br. s, CH_3), 26.2 (s, CH_3-CH), 22.7 (br. s, CH_3-CH). Elemental analysis calcd (%) for $C_{50}H_{66}Cl_4N_6Pd$: C 54.31, H 6.02, N 7.60; found: C 54.18, H 6.14, N 7.44.

Chloro[1-(2,6-diisopropylphenyl)-3-(methyl)-4-(4-tert-butylphenyl)-1,2,3-triazol-5-ylidene]gold(I) (8): Light pink solid (71 mg, 93%). ^{1}H NMR (500 MHz, CD_2Cl_2, 298K): δ (ppm) = 7.76 (d, ^3J(H,H) = 8.4 Hz, 2H, CH_{Ar}), 7.63 (d, ^3J(H,H) = 8.4 Hz, 2H, CH_{Ar}), 7.61 (t, ^3J(H,H) = 8.0 Hz, 1H, CH_{Ar}), 7.36 (d, ^3J(H,H) = 8.0 Hz, 2H, CH_{Ar}), 4.23 (s, 3H, N-CH_3), 2.35 (septet, ^3J(H,H) = 6.7 Hz, 2H, CH-CH_3), 1.40 (s, 9H, CH_3), 1.33 (d, ^3J(H,H) = 6.7 Hz, 6H, CH_3-CH), 1.16 (d, ^3J(H,H) = 6.7 Hz, 6H, CH_3-CH).^{13}C-{^{1}H} NMR (125 MHz, CD_2Cl_2, 298K): δ (ppm) = 161.7 (s, Au-$C_{triazolylidene}$), 154.4 (s, C^{IV}), 147.1 (s, C^{IV}), 145.8 (s, C^{IV}), 135.6 (s, C^{IV}), 131.8 (s, CH_{Ar}), 129.7 (s, CH_{Ar}), 126.5 (s, CH_{Ar}), 124.6 (s, CH_{Ar}), 123.4 (s, C^{IV}), 38.7 (s, N-CH_3), 35.3 (s, C^{IV}), 31.3 (s, CH-CH_3), 29.1 (s, CH_3), 24.5 (s, CH_3-CH), 24.1 (s, CH_3-CH). Elemental analysis calcd (%) for $C_{25}H_{33}AuClN_3$: C 49.39, H 5.47, N 6.91; found: C 49.18, H 5.35, N 7.00.

Chloro(η^4-cycloocta-1,5-diene)[1-(2,6-diisopropylphenyl)-3-(methyl)-4-(4-tert-butylphenyl)-1,2,3-triazol-5-ylidene]iridium(I) (9): Bright yellow solid (64 mg, 85%). ^{1}H NMR (500 MHz, CD_2Cl_2, 298K): δ (ppm) = 7.97 (d, ^3J(H,H) = 8.3 Hz, 2H, CH_{Ar}), 7.60 (d, ^3J(H,H) = 8.3 Hz, 2H, CH_{Ar}), 7.55 (t, ^3J(H,H) = 7.8 Hz, 1H, CH_{Ar}), 7.41-7.28 (m, 2H, CH_{Ar}),4.18-4.15 (m, 2H, CH cod) 4.10 (s, 3H, N-CH_3), 3.28-3.17 (m, 1H, cod), 2.97-2.88 (m, , 1H, CH-CH_3), 2.70-2.62 (m, , 1H, CH-CH_3), 2.01-1.79 (m, 4H, cod), 1.42 (s, 9H, CH_3), 1.30-1.03 (m, 17H, overlapped 12H CH_3-CH and 5H cod). ^{13}C-{^{1}H} NMR (125 MHz, CD_2Cl_2, 298K): δ (ppm) = 171.6 (s, Ir-$C_{triazolylidene}$), 152.8 (s, C^{IV}), 146.0 (s, C^{IV}), 136.3 (s, C^{IV}), 130.9 (s, CH_{Ar}), 130.6 (s, CH_{Ar}), 125.8 (s, C^{IV}), 125.4 (s, CH_{Ar}), 124.5 (s, CH_{Ar}), 81.1 (br. s, CH cod), 80.4 (br. s, CH cod) 50.7 (s, CH_2 cod), 38.0 (s, N-CH_3), 35.1 (s, C^{IV}), 31.3 (s, CH_3), 29.3 (br. s, CH-CH_3), 26.4 (br. s, CH cod), 26.0 (br. s, CH cod), 24.3 (s, CH_3-CH), 23.2 (br. s, CH cod), 22.3 (s, CH_3-CH). Elemental analysis calcd (%) for $C_{33}H_{45}ClIrN_3$: C 55.71, H 6.38, N 5.91; found: C 55.73, H 6.23, N 5.94.

Chlorodicarbonyl[1-(2,6-diisopropylphenyl)-3-(methyl)-4-(4-tert-butylphenyl)-1,2,3-triazol-5-ylidene]rhodium(I) (10): Light yellow solid (60 mg, 99%).^{1}H NMR (500 MHz, CD_2Cl_2, 298K): δ (ppm) = 7.83 (d, ^3J(H,H) = 8.4 Hz, 2H, CH_{Ar}), 7.62 (d, ^3J(H,H) = 8.4 Hz, 2H, CH_{Ar}), 7.58 (t, ^3J(H,H) = 7.8 Hz, 1H, CH_{Ar}), 7.36 (d, ^3J(H,H) = 7.8 Hz, 2H, CH_{Ar}), 4.16 (s, 3H, N-CH_3), 2.58 (septet, ^3J(H,H) = 7.0 Hz, 2H, CH-CH_3), 1.41 (s, 9H, CH_3), 1.34 (d, ^3J(H,H) = 7.0 Hz, 6H, CH_3-CH), 1.10 (d, ^3J(H,H) = 7.0 Hz, 6H, CH_3-CH). ^{13}C-{^{1}H} NMR (125 MHz, CD_2Cl_2, 298K): δ (ppm) = 186.3 (d, ^1J(Rh,C) = 54.4 Hz, CO), 183.8 (d, ^1J(Rh,C) = 74.3 Hz, CO), 165.8 (d, ^1J(Rh,C) = 40.2 Hz, Rh-$C_{triazolylidene}$),153.7 (s, C^{IV}), 147.0 (s, C^{IV}), 146.3 (s, C^{IV}), 136.1 (s, C^{IV}), 131.5 (s, CH_{Ar}), 130.6 (s, CH_{Ar}), 126.1 (s, CH_{Ar}), 124.5 (s, C^{IV}), 124.3 (s, CH_{Ar}), 38.2 (s, N-CH_3), 35.2 (s, C^{IV}), 31.3 (s, CH-CH_3), 29.2 (s, CH_3), 26.3 (s, CH_3-CH), 22.6 (s, CH_3-CH). IR (solid state): ν [cm^{-1}] 2064 (s), 1987 (s). Elemental analysis calcd (%) for $C_{27}H_{35}ClN_3O_2Rh$: C 56.70, H 6.17, N 7.35; found: C 56.65, H 6.28, N 7.35.

Dichloro[1,3-bis(2,6-diisopropylphenyl)-2,4-diphenyl-imidazol-5-ylidene]palladium(II) dimer (11): Yellowish solid (52 mg, 92%). ^{1}H NMR (500 MHz, CD_2Cl_2, 298K): δ (ppm) = 8.09-8.06 (m, 3H, CH_{Ar}), 7.76 (d, ^3J(H,H) = 7.8 Hz, 4H, CH_{Ar}), 7.51-7.35 (m, 12H, CH_{Ar}), 7.20-7.14 (m, 6H, CH_{Ar}), 7.02-6.99 (m, 4H, CH_{Ar}), 6.86 (d, ^3J(H,H) = 7.8 Hz, 3H, CH_{Ar}), 3.63-3.58 (m, 2H, CH-CH_3), 2.56-2.61 (m, 2H, CH-CH_3), 2.19-2.13 (m, 2H, CH-CH_3), 2.06-2.01 (m, 2H, CH-CH_3), 1.38 (d, ^3J(H,H) = 6.8 Hz, 6H, CH_3), 1.28 (d, ^3J(H,H) = 6.8 Hz, 12H, CH_3), 1.10 (d, ^3J(H,H) = 6.8 Hz, 6H, CH_3), 1.07 (d, ^3J(H,H) = 6.8 Hz, 6H, CH_3), 0.35 (d, ^3J(H,H) = 6.8 Hz, 6H, CH_3), 0.28 (d, ^3J(H,H) = 6.8 Hz, 6H, CH_3), 0.16 (d, ^3J(H,H) = 6.8 Hz, 6H, CH_3). Elemental analysis calcd (%) for $C_{78}H_{88}Cl_4N_2Pd_2$: C 65.23, H 6.18, N 3.90; found: C 65.09, H 6.08, N 3.79.

Chloro(η^4-cycloocta-1,5-diene)[1,3-bis(2,6-diisopropylphenyl)-2,4-diphenyl-imidazol-5-ylidene]iridium(I) (13): Bright yellow solid (66 mg, 80%). ^{1}H NMR (500 MHz, CD_2Cl_2, 298K): δ (ppm) = 7.52-7.46 (m, 4H, CH_{Ar}), 7.29-7.21 (m, 8H, CH_{Ar}), 7.10 (t, ^3J(H,H) = 7.8 Hz, 2H, CH_{Ar}), 6.90 (d, ^3J(H,H) = 7.8 Hz, 2H, CH_{Ar}), 2.67 (septet, ^3J(H,H) = 6.9 Hz, 2H, CH-CH_3), 2.59 (septet, ^3J(H,H) = 6.9 Hz, 2H, CH-CH_3), 2.55-2.41 (m, 2H, CH cod), 1.56-1.54 (br. s, 2H, CH cod), 1.41 (d, ^3J(H,H) = 6.9 Hz, 6H, CH_3), 1.34-1.19 (m, 3H, cod), 1.06-1.04 (m, 2H, cod), 0.99 (d, ^3J(H,H) = 6.9 Hz, 6H, CH_3), 0.88-0.85 (m, 3H, cod), 0.82 (d, ^3J(H,H) = 6.9 Hz, 6H, CH_3), 0.81 (d, ^3J(H,H) = 6.9 Hz, 6H, CH_3). ^{13}C-{^{1}H} NMR (125 MHz, CD_2Cl_2, 298K): δ (ppm) = 145.4 (s, C^{IV}), 145.1 (s, $C_{carbene}$-Ir), 143.0 (s, C^{IV}), 142.0 (s, C^{IV}), 136.3 (s, C^{IV}), 131.5 (s, CH_{Ar}), 131.2 (s, C^{IV}), 130.9 (s, CH_{Ar}), 130.8 (s, CH_{Ar}), 129.9 (s, CH_{Ar}), 129.5 (s, CH_{Ar}), 128.6 (s, CH_{Ar}), 128.6 (s, CH_{Ar}), 128.4 (s, CH_{Ar}), 125.7 (s, CH_{Ar}), 125.0 (s, CH_{Ar}), 124.0 (s, C^{IV}), 29.9 (s, CH cod), 29.7 (s, CH cod), 29.2 (s, CH-CH_3), 29.0 (s, CH-CH_3), 25.9 (s, CH_3), 25.8 (s, CH cod), 24.0 (s, CH cod), 23.9 (s, CH_3), 23.7 (s, CH_3), 23.6 (s, CH cod), 23.3 (s, CH cod), 22.7 (s, CH_3). Elemental analysis calcd (%) for $C_{47}H_{56}ClIrN_2$: C 64.39, H 6.44, N 3.20; found: C 64.41, H 6.37, N 3.27.

Chlorodicarbonyl[1,3-bis(2,6-diisopropylphenyl)-2,4-diphenyl-imidazol-5-ylidene]rhodium(I) (14): Light yellow solid (55 mg, 80%). ^{1}H NMR (500 MHz, CD_2Cl_2, 298K): δ (ppm) = 7.53-7.48 (m, 4H, CH_{Ar}), 7.30 (d, ^3J(H,H) = 8.0 Hz, 2H, CH_{Ar}), 7.27-7.20 (m, 6H, CH_{Ar}), 7.06 (t, ^3J(H,H) = 7.8 Hz, 2H, CH_{Ar}), 6.92 (d, ^3J(H,H) = 7.8 Hz, 2H, CH_{Ar}), 2.93 (septet, ^3J(H,H) = 6.8 Hz, 2H, CH-CH_3), 2.54 (septet, ^3J(H,H) = 6.8 Hz, 2H, CH-CH_3), 1.50 (d, ^3J(H,H) = 6.8 Hz, 6H, CH_3), 0.81-0.76 (m, 18H, CH_3). ^{13}C-{^{1}H} NMR (125 MHz, CD_2Cl_2, 298K): δ (ppm) = 186.8 (d, ^1J(Rh,C) = 54.9 Hz, CO), 184.5 (d, ^1J(Rh,C) = 78.0 Hz, CO), 157.9 (d, ^1J(Rh,C) = 42.6 Hz, Rh-$C_{carbene}$), 145.8 (s, C^{IV}), 145.6 (s, C^{IV}), 145.4 (s, C^{IV}), 144.9 (s, C^{IV}), 140.7 (s, C^{IV}), 135.9 (s, C^{IV}), 131.8 (s, CH_{Ar}), 131.5 (s, CH_{Ar}), 131.4 (s, C^{IV}), 130.9 (s, CH_{Ar}), 130.7 (s, CH_{Ar}), 130.3 (s, CH_{Ar}), 128.6 (s, CH_{Ar}), 128.4 (s, CH_{Ar}), 127.8 (s, CH_{Ar}), 125.8 (s, CH_{Ar}), 125.5 (s, CH_{Ar}), 124.1 (s, C^{IV}), 29.9 (s, CH-CH_3), 29.7 (s, CH-CH_3), 29.1 (s, CH_3), 29.0 (s, CH_3),

25.9 (s, CH_3), 24.0 (s, CH_3), 23.8 (s, CH_3), 23.5 (s, CH_3). Elemental analysis calcd (%) for $C_{41}H_{47}ClN_2O_2Rh$: C 66.71, H 6.42, N 3.79; found: C 66.62, H 6.63, N 4.04.

Dichloro[2-(2,6-diisopropylphenyl)-3,3-(dimethyl)-2-azaspiro[4.5]dec-1-ylidene]palladium(II) dimer (15): Orange solid (45 mg, 75%). ^{1}H NMR (500 MHz, CD_2Cl_2, 298K): δ (ppm) = 7.56-7.46 (m, 3H, CH_{Ar}), 7.42-7.31(m, 3H, CH_{Ar}), 3.09-3.02 (m, 2H, H_2C_{Cy}), 2.99-2.86 (m, 4H, CH-CH_3), 2.76-2.69 (m, 2H, H_2C_{Cy}), 2.06-1.98 (m, 4H, CH_2), 1.93-1.83 (m, 7H, H_2C_{Cy}), 1.79-1.72 (m, 4H, H_2C_{Cy}), 1.66-1.53 (m, 5H, H_2C_{Cy}), 1.45-1.34 (m, 12H, CH-CH_3), 1.30-1.18 (m, 24H, 12H C-CH_3 and 12H CH-CH_3). ^{13}C-{^{1}H} NMR (125 MHz, CD_2Cl_2, 298K): δ (ppm) = 234.3 (s, $C_{carbene}$-Pd), 147.4 (s, C^{IV}), 147.2 (s, C^{IV}), 133.8 (s, C^{IV}), 132.5 (s, C^{IV}), 130.0 (br. s, CH_{Ar}), 129.5 (s, CH_{Ar}), 126.2 (br. s, CH_{Ar}), 81.6 (s, C^{IV}), 62.5 (s, C^{IV}), 44.7 (br. s, CH_2), 38.6 (br. s, H_2C_{Cy}), 37.8 (br. s, H_2C_{Cy}), 37.6 (br. s, H_2C_{Cy}), 37.4 (br. s, H_2C_{Cy}), 31.3 (s, CH-CH_3), 30.8 (s, CH-CH_3), 30.5 (s, CH-CH_3), 29.9 (s, CH-CH_3), 29.2 (s, CH_3), 28.9 (s, CH_3-CH), 28.4 (s, CH_3-CH), 27.7 (s, CH_3-CH), 25.9 (s, CH_3-CH), 25.6 (s, CH_3), 25.5 (s, H_2C_{Cy}), 22.7 (s, H_2C_{Cy}), 22.3 (s, H_2C_{Cy}). Elemental analysis calcd (%) for $C_{46}H_{70}Cl_4N_2Pd_2$: C 54.94, H 7.02, N 2.79; found: C 54.73, H 6.84, N 2.83.

Chloro(η⁴-cycloocta-1,5-diene)[2-(2,6-diisopropylphenyl)-3,3-(dimethyl)-2-azaspiro[4.5]dec-1-ylidene]iridium(I) (17): Bright yellow solid (81 mg, 83%). ^{1}H NMR (500 MHz, CD_3CN, 298K): δ (ppm) = 7.47 (t, ^3J(H,H) = 7.8 Hz, 1H, CH_{Ar}), 7.35 (d, ^3J(H,H) = 7.8 Hz, 2H, CH_{Ar}), 3.94 (br. s, 3H, CH cod), 2.87 (septet, ^3J(H,H) = 6.9 Hz, 2H, CH-CH_3), 2.20-2.17 (m, 4H cod), 2.12 (s, 2H, CH_2), 2.02-1.97 (m, 2H, H_2C_{Cy}), 1.89-1.84 (m, 2H, H_2C_{Cy}), 1.72-1.68 (m, 1H, H_2C_{Cy}), 1.63-1.60 (m, 2H, H_2C_{Cy}), 1.57-1.41 (m, 7H, 2H H_2C_{Cy} and 5H cod), 1.33 (s, 6H, C-CH_3), 1.29 (d, ^3J(H,H) = 6.9 Hz, 6H, CH_3-CH), 1.22 (d, ^3J(H,H) = 6.8 Hz, 6H, CH_3-CH). ^{13}C-{^{1}H} NMR (125 MHz, CD_3CN, 298K): δ (ppm) = 249.3 (s, $C_{carbene}$-Ir), 146.3 (s, CH_{Ar}), 135.8 (s, C^{IV}), 130.6 (s, C^{IV}), 125.7 (s, CH_{Ar}), 81.9 (s, C^{IV}), 59.9 (s, C^{IV}), 46.1 (s, CH_2), 36.7 (s, H_2C_{Cy}), 32.2 (s, CH_2 cod), 29.7 (s, CH-CH3), 29.7 (s, CH cod), 27.2 (s, CH_3-CH), 26.1 (s, H_2C_{Cy}), 22.7 (s, H_2C_{Cy}), 22.5 (s, CH_3-CH). Elemental analysis calcd (%) for $C_{31}H_{47}ClIrN$: C 56.30, H 7.16, N 2.12; found: C 56.14, H 7.28, N 2.18.

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[21] CCDC 1016775 (**7**), CCDC 1016774 (**8**), CCDC 1016776 (**9**), CCDC 1016777 (**10**), CCDC 1016778 (**11**), CCDC 1021646 (**13**), CCDC 1016773 (**15**), and CCDC 1016779 (**16**) contain the supplementary crystallographic data**.** 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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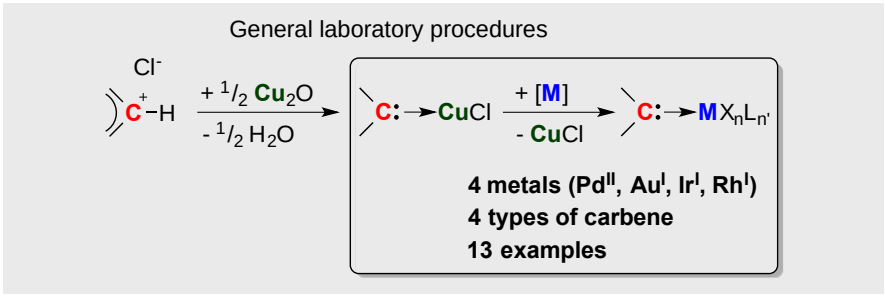

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Generalization of the Copper to Late Transition Metal Transmetallation to Carbenes beyond N-Heterocyclic Carbenes

The NHC-Cu^{I} transmetallation reaction is expanded to Group IX metals, and generalized to other carbenes such as MICs, aNHCs and CAACs to generate a library of transition metal complexes. Since all copper complex precursors are made by direct metallation of easy to handle carbene conjugate acids with copper oxide, the methodology reported here allows for the preparation of a variety of carbene complexes without the use of highly sensitive reagents.