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Imidazolium Carboxylates as Versatile and Selective N-Heterocyclic Carbene Transfer Agents: Synthesis, Mechanism, and Applications

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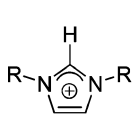
Abstract: *N*,*N*′-Disubstituted imidazolium carboxylates, readily synthetically available, isolable, air- and water-stable reagents, efficiently transfer N-heterocyclic carbene (NHC) groups to Rh, Ir, Ru, Pt, and Pd, to give novel NHC complexes, e.g., $[Pd(NHC)_3OAc]OAc$ and $[Pt(NHC)_3Cl]Cl$ (NHC = 1,3-dimethyl imidazol-2-ylidene). The NHC esters are also effective. Tuning the reaction conditions for NHC transfer can give either mono- or bis-NHCs, or bis- and tris-NHCs. A net N to C rearrangement of the N-alkyl imidazole complex to the corresponding NHC complex was seen with $(MeO)_2CO$ (DMC). DFT calculations identify the steps needed to form the carboxylate from imidazole and DMC: S_N2 methyl transfer from DMC to imidazole, followed by proton transfer from the imidazolium CH to the carboxylate counterion, produces the free NHC H-bonded to MeOH with a weakly associated CO_2. The nucleophilic NHC attacks CO_2 to form NHC−CO_2. NHC transfer to the metal with loss of CO_2 has been calculated for Rh(cod)Cl. A proposed two-*cis*-site reactivity model rationalizes the experimental data: two such vacant sites at the metal are needed to allow coordination of the NHC−CO_2 carboxylate and subsequent CC cleavage with NHC transfer. Partial cod decoordination or chloride loss is thus required for Rh(cod)Cl. Chloride dissociation, calculated to be easier in polar solvent, is confirmed experimentally from the retarding effect of excess chloride.

Introduction

N-Heterocyclic carbene (NHC) complexes are now fully established as an important class of ligands for homogeneous catalysis. While new catalytic applications are frequently reported,[1−5] synthetic routes to NHC complexes still lack full generality and new routes are very desirable. Some common routes include deprotonation of a precursor imidazolium salt (**1**), either by a strong base[6] or by a basic ligand,[7] and oxidative addition of the C−H bond of the imidazolium salt.[8,9] The intermediacy of any free carbene, as in the first route, necessitates dry, air-free conditions and provides only limited tolerance of other functionalities, while direct oxidative addition is only known for a number of specific cases. In an important advance, Lin et al.[10,11] showed that Ag_2O can react with an imidazolium salt to form a Ag−NHC complex that readily transferred the NHC group to palladium and gold. This route has now been extended to give a wide variety of NHC complexes of Rh, Cu, Ru, and Ir.[12−16] While very general, this method can give unexpected products[17] however, such as in the Ag-induced oxidative C−C bond cleavage of the imidazolium precursor of Scheme 1.[18] Thus further methods[19,20] are eagerly sought.



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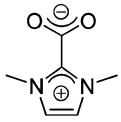

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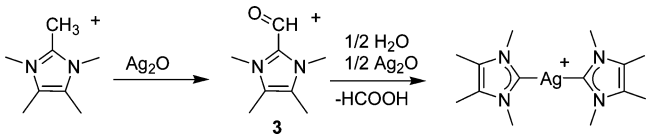
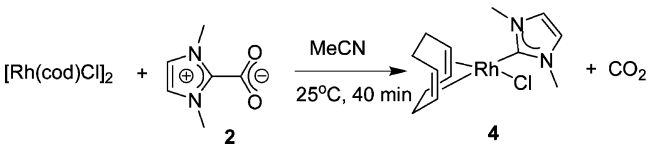
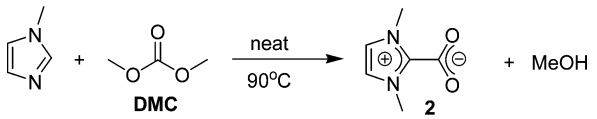
Scheme 1



Scheme 2



Scheme 3

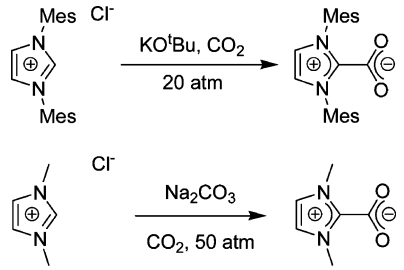


In elucidating our oxidative C−C cleavage pathway of Scheme 1,[18] we found that the acyl imidazoles of type **3** readily transferred the NHC group to Ag^+. Compounds of type **3** are not efficient transfer agents to other, nonoxidizing metals, however. Looking for a more active analogue led us to investigate the reactivity of *N*,*N*′-dimethyl imidazolium-2-carboxylate (NHC−CO_2) (**2**) as an NHC transfer agent to transition metals. Our preliminary report[21] showed that isolable compound **2** indeed transfers the NHC to several metal precursors under mild conditions with release of CO_2 without exclusion of air and water (Scheme 2). This approach has proved useful, and others have reported a successful application of the method.[22,23] We now report further examples of this process, including improved methods for synthesizing a range of analogues of **2** and their esters. The mechanism of the poorly understood formation of **2** from methyl imidazole and $(MeO)_2CO$ (DMC) has now been studied computationally by DFT-(B3PW91) calculations. Calculations on the mechanism of NHC transfer from **2** to Rh(cod)Cl lead to a two-site reactivity model.

Results

Synthesis of NHC−CO_2. The utility of our transfer procedure depends on the availability of a general synthesis of the NHC carboxylates. The prototype *N*,*N*′-dimethyl imidazolium-2-carboxylate can be easily synthesized by a variation of a previously reported procedure[24] involving alkylation of methyl imidazole with $(MeO)_2CO$ (DMC, Scheme 3). This procedure was also found to be general for several monoalkylated imidazoles such as *n*-butyl imidazole (**5**) and isopropyl imidazole, allowing access to the corresponding *N*-methyl, *N*′-alkyl analogues of **2** as intermediates for subsequent transfer to Rh. To escape from the limitation that one N-substituent must be methyl, other very useful syntheses have recently become

Scheme 4



available from the imidazolium salt. Louie and co-workers,[25] Tommasi and co-workers,[26] and Delaude and co-workers[23] have reported such syntheses, e.g., of *N*,*N*′-di(mesityl)imidazolium-*2*-carboxylate, using base and in some cases a high pressure of CO_2 (Scheme 4).

In an unexpected complication, variation of temperature in the DMC reaction of Scheme 3 alters the isomeric product ratio of 2- to 4-carboxylate: below 95 °C the 2-carboxylate predominates (>95%), while above 120 °C the 4-carboxylate is mainly obtained (>90%). For this reason, we have slightly modified the Louie conditions in our work by using a temperature of 90 °C to obtain the 2-carboxylate. The symmetrical diethyl or dibenzyl carbonates have proved unsuccessful alkylating agents for *N*-methylimidazole under the same conditions.

Synthesis of *N*,*N*′-Disubstituted Imidazolium Carboxylate Esters. A wider variety of NHC transfer agents can be prepared using the related carboxylate esters because these can be reliably prepared from the corresponding imidazolium salts. As reported in our initial communication,[21] we find that NHC esters (NHC−CO^iBu) are easily synthesized by the deprotonation of the appropriate imidazolium precursor by KO^tBu followed by treatment with freshly distilled isobutyl chloroformate (Scheme 5). This procedure has been successfully carried out for bis-mesityl and bis-isopropyl cases. Ester **6** is capable of transferring the corresponding NHC to Rh and Ir and provides a storable, convenient NHC transfer agent that, like the imidazolium carboxylates, does not require exclusion of air and water. This allows extension of the method beyond the cases discussed above. Of course, the use of the strong base in the synthesis of the ester is a disadvantage, but NHC transfer is possible under the same mild conditions, presumably with concomitant hydrolysis and formation of the corresponding carboxylate as an intermediate.

DFT Study of Formation of NHC−CO_2, 2. The reaction between methyl imidazole and $(MeO)_2CO$ (DMC) to form NHC−CO_2, **2**, previously unknown, was studied computationally for *N*-methylimidazole via DFT with the hybrid B3PW91 functional. It has not of course been possible to explore the entire potential energy surface, but a realistic three-step pathway has been proposed based on the computational data. In the first step, rate-determining methyl transfer from DMC to imidazole gives an ion pair consisting of the cationic alkylated imidazolium ion and the $MeOCO_2$ counterion. In the second step, a proton transfer within the imidazolium/carboxylate ion pair induces the C−O bond cleavage between NHC and CO_2 with concomitant formation of MeOH. Finally the third step consists of the nucleophilic attack of NHC to CO_2 to form the new C−C bond.

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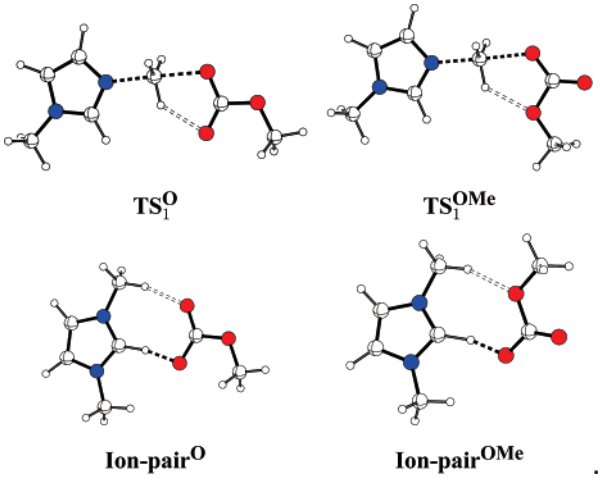


Figure 1. Optimized geometry for the two transition states for S_N2 methyl transfer from DMC to methyl imidazole and the corresponding products of reaction. $\mathbf{TS_1^O}$ is favored over $\mathbf{TS_1^{OMe}}$.

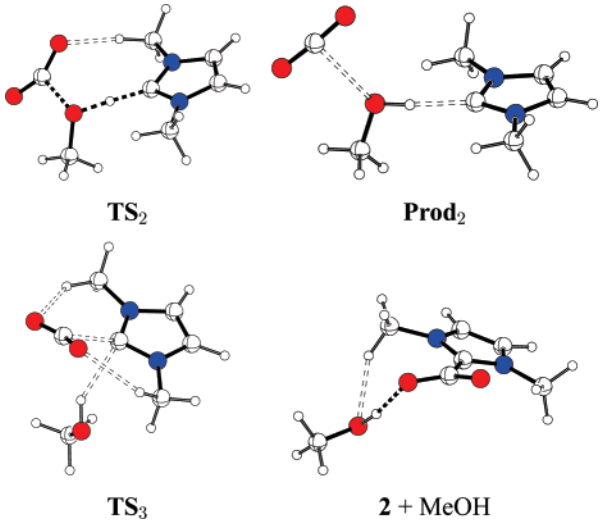


Figure 2. Optimized geometries for the transition states and the products corresponding to the C−O bond cleavage (top) and C−C bond formation (bottom) in the reaction of imidazole with DMC to form NHC−CO_2 and methanol.

The reaction of Scheme 3 in which reactants and products are considered as isolated molecules in the gas phase is calculated to be endothermic by 9.4 kcal mol^{-1}. Although slightly disfavored thermodynamically, the equilibrium is shifted to the right by precipitation of **2** from the reaction medium. Furthermore, inclusion of an H-bond between the NHC−CO_2 and CH_3OH products gives a significant additional stabilization. The energy of reaction is then calculated to be −2.0 kcal mol^{-1}. The methyl group transfer from DMC to the imidazole nitrogen follows a classic S_N2 mechanism. Two transition states, $\mathbf{TS_1^O}$ and $\mathbf{TS_1^{OMe}}$, have been located with an energy barrier of $\Delta E^{\ddagger}$ = 32.2 and 37 kcal mol^{-1} above separated methyl imidazole and DMC, respectively. The transition state geometries are typical of an S_N2 mechanism (Figure 1), with an almost planar CH_3 group located at similar distances from both nucleophiles (C...O = 2.027 Å, C...N = 1.845 Å, $\mathbf{TS_1^O}$; C...O = 2.035 Å, C...N = 1.831 Å, $\mathbf{TS_1^{OMe}}$). At the two transition states, an extra stabilizing interaction develops between one H atom of CH_3 and the closest oxygen atom (H...O = 1.994 Å, $\mathbf{TS_1^O}$; H...OMe = 2.059 Å, $\mathbf{TS_1^{OMe}}$). This H-bonding interaction is stronger with the carbonate oxygen in $\mathbf{TS_1^O}$ than with the methoxy oxygen in $\mathbf{TS_1^{OMe}}$, thus favoring the former.

Several H-bonds are also present in the $MeIm^+/O_2COMe^-$ ion pair (Figure 1) resulting from the S_N2 step (MeIm = *N*,*N*′-dimethyl imidazolium). A strong H-bond between the acidic C2−H on MeIm and one carboxylate O is accompanied by a weaker one between a N−Me CH bond and the second carboxylate oxygen in $\mathbf{Ion\text{-}pair^O}$ or the methoxy group in $\mathbf{Ion\text{-}pair^{OMe}}$. The 3.8 kcal mol^{-1} lower stability of the latter comes from the lower basicity of methoxy vs carboxylate oxygen. Short H-bond distances indicate stronger interactions in $\mathbf{Ion\text{-}pair^O}$ (C2−H = 1.155 Å, (C2)H...O = 1.55 Å, (N-methyl)CH...O = 1.965 Å) than in $\mathbf{Ion\text{-}pair^{OMe}}$ (C2−H = 1.209 Å, (C2)H...O = 1.403 Å, (N-methyl)CH...O = 2.277 Å). The carboxylate next slides along the imidazolium to create the strongest possible H-bond with C2−H, thus leading to $\mathbf{Ion\text{-}pair^O}$ from $\mathbf{TS_1^O}$ and to $\mathbf{Ion\text{-}Pair^{OMe}}$ from $\mathbf{TS_1^{OMe}}$. The formation of $\mathbf{Ion\text{-}pair^O}$ is marginally exothermic from separated reactants (ΔE = −1.1 kcal mol^{-1}), and that of $\mathbf{Ion\text{-}pair^{OMe}}$ is very slightly endothermic (ΔE = 2.7 kcal mol^{-1})

From $\mathbf{Ion\text{-}pair^{OMe}}$, the carbonate slides along the imidazolium to reach $\mathbf{TS_2}$ where a proton transfers from the imidazolium to the methoxy group of the carboxylate anion with an energy barrier of $\Delta E^{\ddagger}$ = 12.2 kcal mol^{-1} relative to the ion pair (Figure 2). This transition state is associated with simultaneous cleavage of the C2−H and O_2C−OMe bonds to form the NHC, MeOH, and CO_2. Proton transfer from $\mathbf{Ion\text{-}pair^O}$ would protonate an oxygen of the CO_2^- group, an unfavorable path for CO_2 formation. Thus $\mathbf{Ion\text{-}pair^O}$, a kinetically accessible intermediate, needs to rearrange to $\mathbf{Ion\text{-}pair^{OMe}}$, an intermediate on the reaction path and no more than 4 kcal mol^{-1} higher in energy. At $\mathbf{TS_2}$, the transferring H^+ is not far from being midway between C2 and O (C2...H = 1.361 Å and O...H = 1.219 Å). CO_2 formation is significantly advanced with a distance of 1.802 Å between the C of the nascent CO_2 and O of the nascent methanol (vs 1.419 Å in $\mathbf{Ion\text{-}pair^{OMe}}$). The O−C−O angle is 148°, opened up from 130.5° in $\mathbf{Ion\text{-}pair^{OMe}}$. This transition state leads to a species, $\mathbf{Prod_2}$ (Figure 2), in which the NHC and MeOH interact via an H-bond (C2...H = 1.833 Å, O−H = 1.001 Å) and a CO_2 molecule weakly interacts with the methanol oxygen atom (O...C = 2.665 Å). The transformation from $\mathbf{Ion\text{-}pair^{OMe}}$ to $\mathbf{Prod_2}$ is slightly endothermic (ΔE = 4.7 kcal mol^{-1}).

Breaking the O−H...C2 interaction in $\mathbf{Prod_2}$ leads to $\mathbf{TS_3}$, corresponding to the coupling between the NHC and CO_2 (Figure 2). The distance between (MeO)−H and C2 is now 2.207 Å, and the MeOH has moved out of the carbene plane. This results in CO_2 oxygen interacting with the N-methyl CH bond (OCO...HC = 2.330 Å and 2.266 Å), with the CO_2 moving into the carbene plane as appropriate for subsequent carboxylate formation (C...C2 = 2.165 Å). This supramolecular network leads to an easy coupling process with an energy barrier of only $\Delta E^{\ddagger}$ = 8.4 kcal mol^{-1} (Figure 3). The product of the reaction is NHC−CO_2 (**2**) in an H-bonded adduct with a methanol molecule (Figure 2). A short O−H...O contact (1.760 Å) is supplemented by an O...CH_3 interaction with a N-methyl CH bond (2.187 Å).

The low barrier for this key nucleophilic attack of NHC on CO_2 explains the experimental observation that the yield of NHC−CO_2 is only slightly reduced (to 66% from 82%) when the DMC/methylimidazole reaction is performed under reflux with a flow of N_2 through the reaction mixture instead of in a

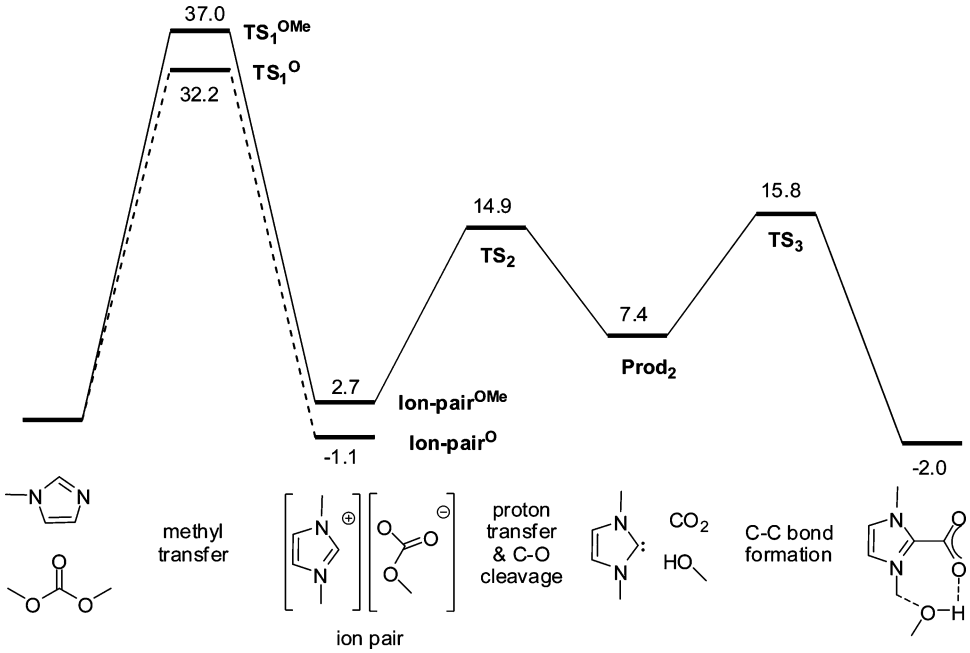


Figure 3. Energy diagram (kcal mol^{-1}) for the organic synthesis of NHC−CO_2. Separated methyl imidazole and DMC serve as the origin for the energies.

Table 1. NHC Metal Complexes Obtained from Reaction of Metal Salts with *N,N′*-Dimethyl Imidazolium Carboxylate (**2**)

entry	reactant	product	time (h)	yield % (lit.)[a]
1	$[Rh(cod)Cl]_2$	Rh(cod)(NHC)Cl[b] (**4**)	0.5	93 (91)[a]
2	$[Ir(cod)Cl]_2$	Ir(cod)(NHC)Cl[b] (**7**)	0.5	82 (90)[a]
3	$[(ArH)RuCl_2]_2$ (**8**)	$(ArH)RuCl_2(NHC)$[c] (**9**)	2	85 (90)[a]
4a	$[Ir(cod)(PPh_3)_2]PF_6$ (**10**)	$[Ir(cod)(NHC)_2]PF_6$[d] (**11**)	2	84
4b	$[Ir(cod)(PPh_3)_2]PF_6$ (**10**)	$[Ir(cod)(PPh_3)(NHC)]PF_6$[b] (**12**)	2	89
5a	$Ir(cod)(py)_2]PF_6$	$[Ir(cod)(NHC)_2]PF_6$[d] (**11**)	1	76
5b	$Ir(cod)(py)_2]PF_6$	$[Ir(cod)(py)(NHC)]PF_6$[b] (**13**)	1	78
6	$Pd(OAc)_2$	$[Pd(NHC)_3(OAc)]OAc$[c] (**14**)	12	71
7	$PdCl_2(MeCN)_2$	$[Pd(NHC)_3(Cl)]Cl$[c] (**15**)	12	65
8	K_2PtCl_4	$[Pt(NHC)_3Cl]Cl$[c] (**16**)	28	76
9	$IrCl(CO)(PPh_3)_2$	$[Ir(PPh_3)_2(CO)(NHC)]Cl$[c] (**17**)	6	79

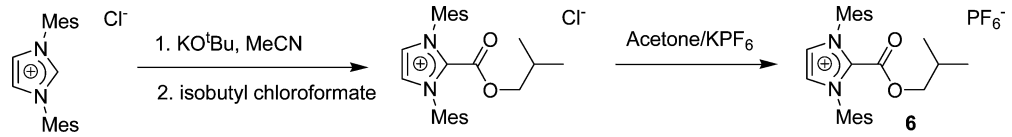
[a] By the traditional free carbene route. [b]Conditions: MeCN, 25 °C. [c]Conditions: MeCN, 75 °C; NHC = 1,3-dimethylimidazol-2-ylidene (1 equiv), cod = 1,5-cyclooctadiene; ArH = η^6-*p*-cymene; py = pyridine. [d]Conditions same as those in footnote c but with 2 equiv of NHC−CO_2.

closed vial. This suggests that CO_2 is efficiently scavenged and may not even readily escape from the cage in which it is formed.

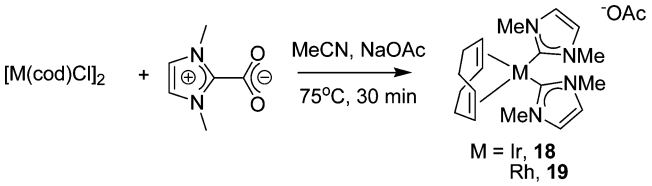
The transformation (Figure 3) of methyl imidazole and DMC to **2** and MeOH is exothermic by 2 kcal mol^{-1} in the H-bonded product pair and slightly endothermic by 9.4 kcal mol^{-1} without this interaction. The polar nature of NHC−CO_2 and the anionic character of the oxygens give rise to a large H-bond stabilization. The rate-determining step for the formation of NHC−CO_2 is the methyl transfer from DMC to the imidazole nitrogen atom with an energy barrier of around 35 kcal mol^{-1} (Figure 3). The subsequent bond cleavage (C2−H, O−C) and bond forming (C−C, O−H) steps have lower energy barriers of ca. 10 kcal mol^{-1}. Although it is not possible to quantify the stabilization associated with all of the supramolecular H-bonding interactions, they are certainly important in keeping the transition states and intermediates at a relatively low energy. Consistent with the experimental failure of diethyl carbonate to react, the barrier was calculated to be 2.7 kcal/mol higher in this case.

NHC Transfer to Metal Centers. Transfer of NHCs from the NHC−CO_2 precursors in refluxing acetonitrile has been investigated for a variety of metal complexes of the late transition metals (Table 1). In the case of $[M(cod)Cl]_2$, (M = Rh, Ir), the reaction yields M(cod)(NHC)Cl with cleavage of the chloro bridges (Table 1, entries 1−2). The same bridge cleavage occurs for the conversion of $[(\eta^6\text{-ArH})RuCl_2]_2$ to the mono NHC derivative (entry 3). It is also possible to displace one or two neutral ligands from Ir(I) such as PPh_3 (entry 4) and pyridine (entry 5). Room-temperature conditions using 1 equiv of the carboxylate yield the mono-NHC complexes (entries 4b and 5b). In contrast, at 75 °C with 2 equiv of carboxylate, both neutral ligands are displaced to give the bis-NHC derivatives (entries 4a and 5a). The carboxylate reagent is therefore extremely selective for the formation of either compound with appropriate conditions. The d^8 square planar precursors $Pd(OAc)_2$, $PdCl_2(MeCN)_2$, and K_2PtCl_4 also react to give the unusual tris-NHC derivatives with displacement of all but one of the anionic ligands (entries 6 to 8). Entries 1−4 of Table 1, where the precursors and products are air-stable, give equally good NHC transfer results in air or N_2. This makes the procedure particularly convenient. For the less reactive precursors of entries 6−8, exclusion of water is needed to prevent slow decomposition of the carboxylates to the imidazolium salts. Vaska's complex (entry 9) gives substitution of the Cl, perhaps because of the high trans effect of CO. The imidazolium-4-carboxylates do not transfer efficiently to any of the precursors shown in Table 1.

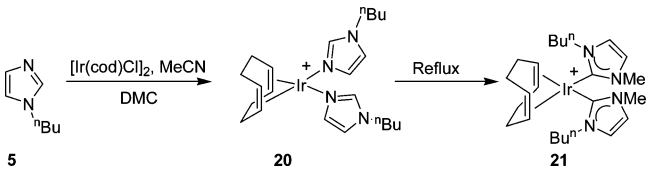
Scheme 5



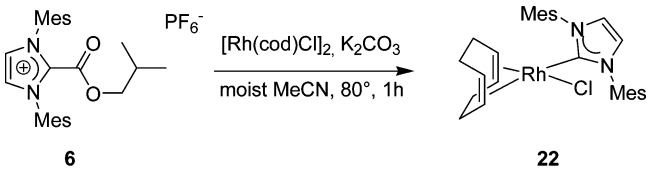
Scheme 6



Scheme 7



Scheme 8



The complexes were characterized by NMR spectroscopy and elemental analysis as well as, for known compounds, by comparison with authentic materials prepared according to standard methods. For $[Pd(NHC)_3(OAc)]OAc$ (**14**), an X-ray structure was also obtained, as reported in the communication.[21]

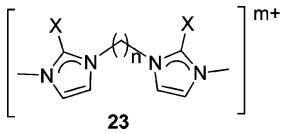
The addition of NaOAc to the medium modifies the results of entries 1 and 2 in Table 1. Instead of the mono-NHC products normally formed, the acetate labilizes the chloride ligands in $[M(cod)Cl]_2$ to give $[(cod)M(NHC)_2]OAc$ within minutes as the final product in >90% isolated yield (Scheme 6). Once again high selectivity can be achieved. Likewise, although reactions with the simple chloride salts $RhCl_3$, $IrCl_3$, and $RuCl_3$ without any additives did not yield any product, upon addition of a stoichiometric amount of sodium acetate, a mixture of mono- and bis-NHC products of these metals is formed. However these reactions have not so far proved synthetically useful because mixtures of products are always obtained. The asymmetrically substituted carboxylates mentioned earlier, such as *N*-methyl-*N*′-*n*-butylimidazolium-2-carboxylate, can also be efficiently transferred to the same metals in a similar fashion.

N to C Rearrangement of N-Alkyl Imidazole to NHC. Several recent reports of N-donor to C-donor rearrangements of imidazoles to NHCs have attracted attention.[27] We now report similar chemistry (Scheme 7) that also helps lift the limitation to N-methyl NHCs. This useful two-step, one-pot route to NHC complexes goes via $[M(cod)L_2]^+$ (L = *N*-butyl imidazole), readily formed from $[Rh(cod)Cl]_2$ or $[Ir(cod)Cl]_2$. The subsequent reaction with DMC gives the corresponding NHC complexes in good yields (Scheme 7). The method gives not only high yields but also more easily isolated products by removal of excess DMC and byproducts by treatment with diethyl ether. Bis-NHC products were also observed for *N*-isopropyl imidazole, but monosubstituted [M(cod)Cl(NHC)], for the bulky *N*-adamantyl imidazole, presumably due to steric effects.

Initial formation of the known *N*-bound bisimidazole cations **20** was confirmed by NMR and mass spectroscopic studies. The imidazole probably dissociates, undergoes carboxylation and methylation as in Scheme 3, and then reacts as in Table 1 entry 5a.

Transfer of NHC Carboxylate Esters to Metal Precursors. To broaden the applicability of the method still further to cover a wider range of NHCs, we looked at the corresponding NHC esters. These are readily available from the imidazolium salt, base, and isobutyl chloroformate as described above. Indeed, carboxylate esters such as **6** are also able to transfer the NHC to $[Rh(cod)Cl]_2$ to give [Rh(cod)(NHC)Cl] (Scheme 8), presumably after hydrolysis to the carboxylate *in situ*. We find that the presence of K_2CO_3 in the medium facilitates the transfer, possibly by assisting the hydrolysis of the ester. Adventitious water is always present in the solvents and glassware, but deliberate addition of water does not seem to enhance the yield and deliberate drying does not completely suppress the reaction. Even so, the reaction times for the esters are considerably longer than those for the carboxylates (60 min vs 15 min), consistent with the need for slow hydrolysis. The bulky mesityl groups only permit monosubstitution in this case (Scheme 8).

Initial attempts to apply the ester method to chelating NHCs have so far proved unsatisfactory. The appropriate precursors, **23** ($n = 1, 2, 3$; X = H; $m = 0$), gave the diesters (X = COO^i-Bu; $m = 2$) in poor yield, and the subsequent transfer reactions to Rh and Ir were not clean.



23

Carboxylate Is the Active Transfer Agent. To eliminate the possibility that the NHC−CO_2 first loses CO_2 to give the free NHC which only then transfers NHC, we showed that the reaction in entry 1 (Table 1) proceeds normally in H_2O/MeCN (90:10 v/v), which would be expected to protonate any intermediate free NHC to give the imidazolium salt. To eliminate the further possibility that the imidazolium salt that would result from decarboxylation and protonation of **2** was the true transfer agent, we looked at the reaction of the same metal precursors with *N*,*N*′-dimethyl imidazolium bromide. In all but one case, no NHC complex was formed, but $Pd(OAc)_2$ did yield $PdBr_2$-

(27) (a) Lewis, J. C.; Bergman, R. G.; Ellman, J. A. *J. Am. Chem. Soc.* **2007**, *129*, 5332−5333. (b) Burling, S.; Mahon, M. F.; Powell, R. E.; Whittlesey, M. K.; Williams, J. M. J. *J. Am. Chem. Soc.* **2006**, *128*, 13702−13703. (c) Esteruelas, M. A.; Fernandez-Alvarez, F. J.; Oñate, E. *J. Am. Chem. Soc.* **2006**, *128*, 13044−13045. (d) Sini, G.; Eisenstein, O.; Crabtree, R. H. *Inorg. Chem.* **2002**, *41*, 602−604.

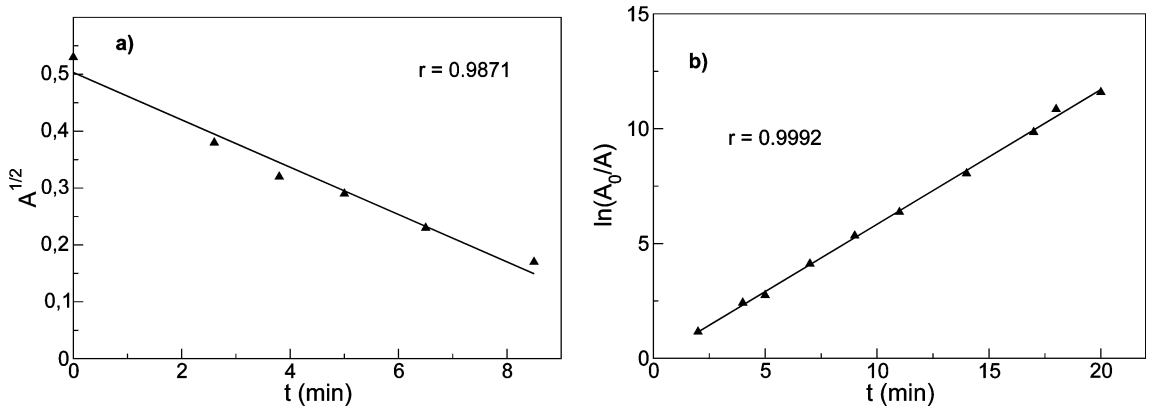


Figure 4. (a) Plot of square root of concentration of $[Rh(cod)Cl]_2$ as a function of time showing half order behavior with respect to Rh dimer (Scheme 2). (b) Plot showing first-order relationship for decay of **24** on reaction with $[Rh(cod)Cl]_2$.

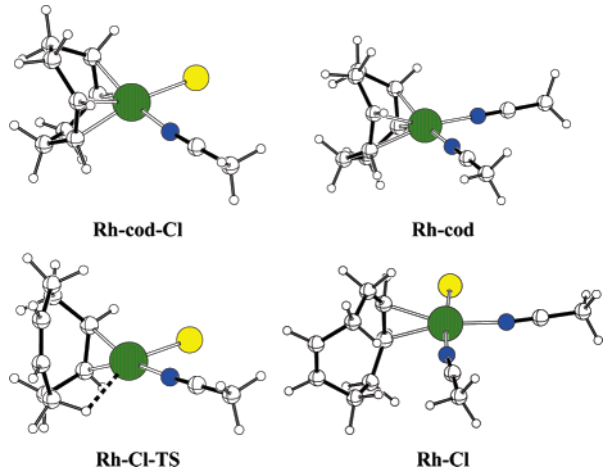


Figure 5. Structures of the acetonitrile-stabilized Rh(cod)Cl complexes.

$(NHC)_2$, a reaction that has previously been reported.[28] This is a different product than is formed from NHC−CO_2, however, so the intermediacy of the imidazolium salt is unlikely even here.

In the case of less active metal precursors, such as $Pd(OAc)_2$ and K_2PtCl_4, the reaction takes 6−28 h. Attempts to accelerate it by reflux (82 °C) were unavailing because the carboxylate decomposes slowly under these conditions and the resulting NHC protonates to give the imidazolium salt, which is ineffective as an NHC transfer agent, thus significantly decreasing the yield of NHC complex.

Kinetic Studies. If the dissociation equilibrium of $[Rh(cod)Cl]_2$ is assumed to be fast, then the rate law for $[Rh(cod)Cl]_2$ reacting with NHC−CO_2 can be written as $v = k_{obsd}$[NHC−CO_2][$[Rh(cod)Cl]_2]^{1/2}$. To check the validity of this rate law, kinetic studies (see Experimental Section) were conducted on the reaction of Scheme 2 using $[Rh(cod)Cl]_2$ and the more soluble 1-methyl-3-butyl imidazolium carboxylate (**24**). When **24** was introduced in excess, the reaction was shown to be half order with respect to $[Rh(cod)Cl]_2$ (Figure 4), and when the Rh dimer was in excess, data indicated that the reaction is first order with respect to the carboxylate, as illustrated in Figure 4. The addition of chloride (NBu_4Cl, 0.1 M) strongly inhibited the NHC transfer. The kinetics of $[Rh(cod)Cl]_2$'s disappearance was unaffected by the Cl ion, but the half time of NHC transfer became about three times as long. Solubility problems prevented quantitative interpretation in terms of reaction order.

NHC Transfer to the Metal Fragment: Computational Study for the Rh(cod)Cl System. The mechanism for NHC transfer from NHC−CO_2, **2**, to Rh has been studied computationally for Rh(cod)(Cl), a choice which allows us to consider both neutral and cationic cases.[29] The geometry optimizations were performed at the B3PW91 level for molecules in the gas phase. The reactions proceed via dissociation of neutral or anionic ligands from Rh, either cod or chloride. Comparison between these two processes required us to consider the influence of the solvent, especially important in the case of chloride. The solvent (CH_3CN) has been considered through single-point PCM calculations on the gas-phase geometries. In addition, an empty coordination site formed by departure of a ligand (cod or Cl) may be occupied by the solvent. For this reason, the necessary numbers of CH_3CN molecules are introduced in the modeling when needed.

Forming Two Empty Coordination Sites at the Metal. The dissociation of the dinuclear Rh complex, $[Rh(cod)Cl]_2$, in acetonitrile to form the solvento-stabilized monomer $Rh(cod)Cl(NCCH_3)$, **Rh-cod-Cl** (Figure 5), consistent with the kinetics, is calculated to be essentially thermoneutral after allowing for acetonitrile coordination and continuum stabilization via the PCM approach ($\Delta E = -1.9$ kcal mol^{-1}). The monomer **Rh-cod-Cl** is then used as a reference for the energies of all the species involved in the reaction. The NHC transfer from **2** to Rh needs two vacant sites at Rh: one to anchor the substrate through O-coordination, and one to create the new Rh−C2 bond with the NHC ligand. No reaction path could be identified from **Rh-cod-Cl** which has only one coordination site. The complexes with two solvent-stabilized vacant sites corresponding to partial dissociation of the cod ligand (η^2-cod) denoted **Rh-Cl**, or dissociation of Cl^- denoted **Rh-cod**, have therefore been optimized (Figure 5).

Opening the cod ligand to allow for a second acetonitrile ligand to coordinate and form **Rh-Cl** is 19.3 kcal mol^{-1} uphill. The transition state, **Rh-Cl-TS** (Figure 5), corresponding to cod opening has been located on the potential energy surface 47 kcal mol^{-1} above **Rh-cod-Cl**. The structure of the transition

(28) Hermann, W. A.; Elison, M.; Fischer, J.; Kocher, C.; Artus, G. R. J. *Angew. Chem., Int. Ed.*, **1995**, *34*, 2371−2374.

(29) Computational studies did not address transfer of NHC from the 4-carboxylate, because all experimental attempts to obtain the 4-NHC complexes in this way failed. Transfer from the 4-carboxylate should be less favored because of the higher C−C bond energy associated with the more nucleophilic 4-NHC.

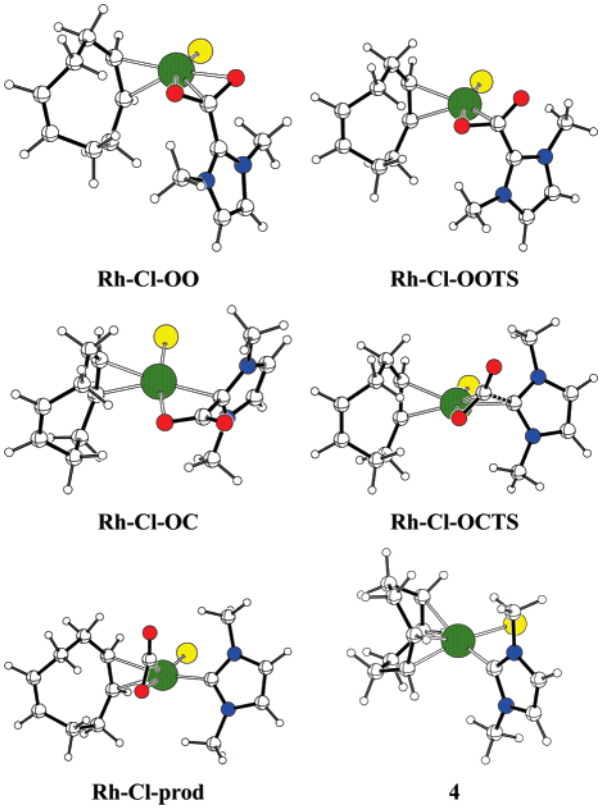


Figure 6. Optimized geometry of minima and transition states for the formation of the Rh−NHC bond from **Rh-Cl** and NHC−CO_2.

state features an agostic interaction between one methylene group and the Rh center with typical metric parameters (Rh...H = 2.130 Å, C−H = 1.124 Å). This interaction slightly stabilizes the transition state. Nevertheless, the energy barrier for cod opening is relatively high, and heating is required to overcome it. Coordination of the second MeCN could certainly lower this barrier, but the transition state for cod decoordination via such an associative step was not sought. Partial decoordination of cod, a well-established fact,[30] is not the focus of this study.

Forming Rh(cod)Cl(NHC) via Partial Cod Decoordination; Unusual η^3-NHC−CO_2 Coordination Mode. In **Rh-Cl**, substitution of the two acetonitriles by NHC−CO_2, **2**, affords the complex **Rh-Cl-OO** having a highly unusual η^3 structure. NHC−CO_2 is coordinated to Rh via the carbon and the two oxygen atoms, featuring an allyl-type coordination of the carboxylate part of NHC−CO_2 (Figure 6). The geometry at Rh is square planar with the coordinated cod C═C bond perpendicular to the coordination plane and the η^3 NHC−CO_2 in the molecular plane. The Rh−O bond nearly trans to Cl is longer than the Rh−O bond trans to the cod C═C bond (2.235 vs 2.150 Å). The carbon atom of the carboxylate lies below the coordination plane at 2.091 Å from Rh. The substitution of the two MeCN groups by η^3-NHC−CO_2 is endothermic by +14.9 kcal mol^{-1} suggesting that NHC−CO_2 is a weaker ligand than two MeCN groups. The η^3 coordination of NHC−CO_2 allows only for a relatively weak interaction between the oxygen centers and Rh and is far from the usual κ^2-coordination of carboxylate groups. The traditional κ^2-σ coordination with M, O, O and C all coplanar is prevented here by the steric clash between the NHC methyl group and the dangling double bond of the η^2-cod. All experimental attempts to securely identify such intermediates in the reaction failed, although in situ NMR spectra showed small transient peaks for unidentifiable intermediates.

From this adduct, isomerization to the less stable (3.7 kcal mol^{-1}) **Rh-Cl-OC** intermediate occurs with a low-energy barrier (10.4 kcal mol^{-1}) through the transition state denoted **Rh-Cl-OOTS** (Figure 6). The transition for isomerization is associated with the loss of one Rh−O interaction (Rh...O = 2.856 Å) and π-coordination of the other CO bond in the coordination plane (Rh−O = 2.189 Å, Rh−C = 2.217 Å, C═O = 1.29 Å). The geometry of the transition state is best described as a slightly distorted T-shaped ML_3 fragment with two double bonds, C═C of cod and CO of the carboxylate, coordinated perpendicularly. The C2 carbon of the NHC is well positioned to approach the empty coordination site of the metal in the crucial transfer step. The isomerization product, **Rh-Cl-OC**, is a four-membered metallacyle with a square planar geometry, O trans to Cl (Rh−O = 2.123 Å) and the C2 atom of the NHC group at 2.198 Å from Rh (Figure 6). The carboxylate carbon atom is no longer coordinated (Rh...C = 2.611 Å) but takes the β position in the metallacycle, and the NHC ring is perpendicular to the coordination plane. The geometry of **Rh-Cl-OC** is ideally suited for C−C bond cleavage.

The transition state structure, **Rh-Cl-OCTS** (Figure 6), associated with C−C bond cleavage, lies 6.9 kcal mol^{-1} above **Rh-Cl-OC**. The Rh−O and Rh−C2 distances of 2.165 Å and 2.153 Å, respectively, are still close to the values in **Rh-Cl-OC**. The main difference from **Rh-Cl-OC** is a decrease in the distance between Rh and the β carbon of the CO_2 fragment (2.258 Å in **Rh-Cl-OCTS** vs 2.611 Å in **Rh-Cl-OC**) and an increase of the CC distance between the NHC and the CO_2 fragments (1.743 Å at the transition state vs 1.551 Å in **Rh-Cl-OC**) indicating the formation of the Rh−C bond and the associated cleavage of the CC bond. The geometry of the carboxylated NHC ligand in **Rh-Cl-OCTS** is best described as a C−C−O allyl-type coordination. The transition state **Rh-Cl-OCTS** leads to **Rh-Cl-prod**, a square planar complex, in which the CC bond of NHC−CO_2 is fully broken, the NHC is now coordinated to the metal and CO_2 is π-bonded to the metal via one C═O bond (Figure 6). The complex **Rh-Cl-prod** is 20.0 kcal mol^{-1} more stable than **Rh-Cl-OC** indicating that the CC cleavage is an exothermic step. CO_2 is not a good ligand, and substitution by the dangling cod double bond is strongly exothermic (−25.4 kcal mol^{-1}), leading to the product Rh(cod)(Cl)(NHC), **4** (Figure 6). No attempt was made to optimize a transition state for displacement of CO_2 by the cod C═C bond. The overall reaction (see Figure 7) from separated **Rh-cod-Cl** and NHC−CO_2 to Rh(cod)(Cl)(NHC) and CO_2 is exothermic by −7.5 kcal mol^{-1}, and the rate-determining step is the opening of the cod ligand to create a total of two vacant sites.

Forming Rh(cod)Cl(NHC) Bond by Loss of Chloride. In an alternate pathway, that appears to be distinctly more favored in a polar solvent such as MeCN, chloride dissociates. The substitution of Cl^- with CH_3CN leads to a cationic complex **Rh-cod** with two coordinated MeCN ligands and free Cl^- (Figure 5) calculated to be only 2.4 kcal mol^{-1} above neutral **Rh-cod-Cl** if the stabilizing effect of the solvent MeCN is included via the continuum model. Coordination of the NHC−

(30) Hanasaka, F.; Tanabe, Y.; Fujita, K.; Yamaguchi, R. *Organometallics* **2006**, *25*, 826−831.

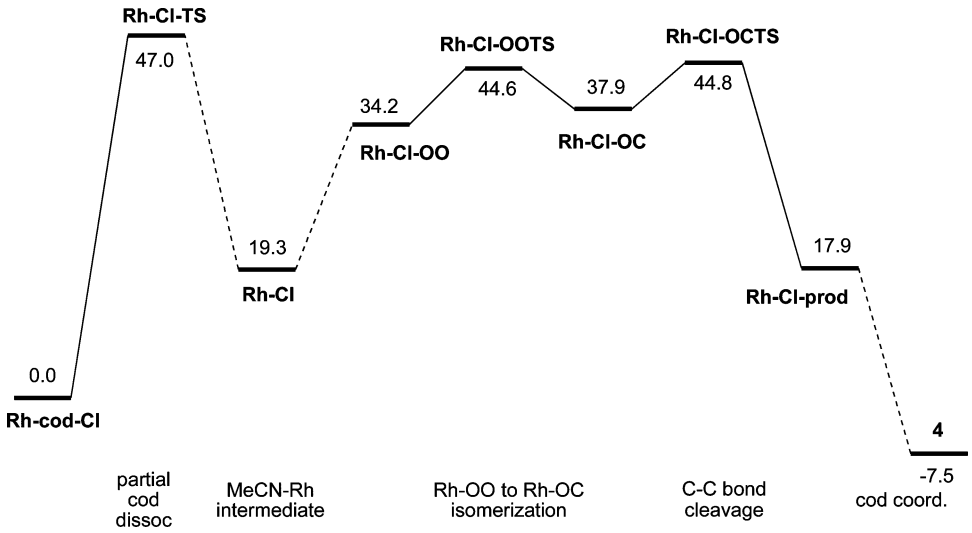


Figure 7. Energy profile (kcal mol^{-1}) for the pathway involving partial decoordination of cod. Dotted lines involve steps with gain or loss of MeCN.

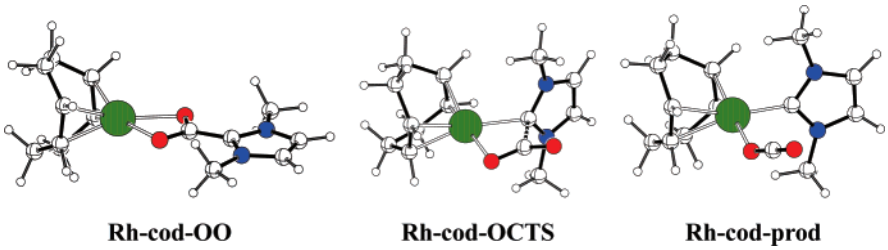


Figure 8. Optimized geometry of minima and transition states for the formation of the Rh−NHC bond from **Rh-cod** and NHC−CO_2.

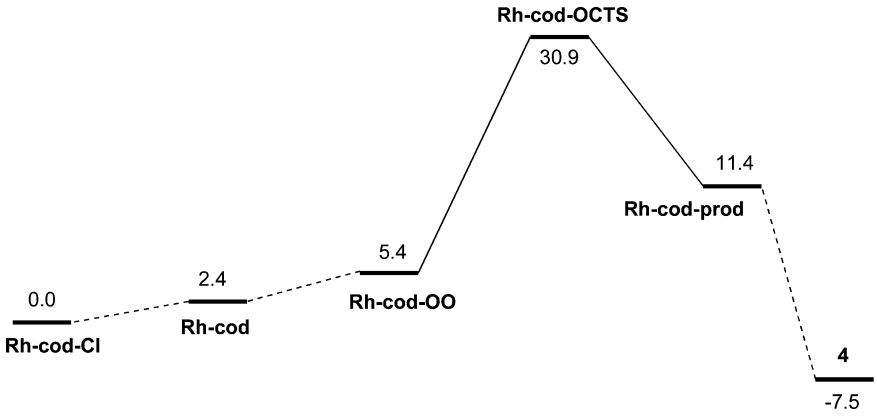


Figure 9. Energy profile (kcal mol^{-1}) for the chloride dissociation pathway. Dotted lines involve steps with gain or loss of MeCN.

CO_2 carboxylate is thermodynamically favored and gives **Rh-cod-OO**, which lies only 3 kcal mol^{-1} above **Rh-cod**. The coordination of the NHC−CO_2 is the usual κ^2-type with two identical Rh−O σ bonds (2.223 Å). The carboxylate lies in the molecular plane putting the carbon 2.52 Å from Rh (Figure 8). The NHC ring lies in the coordination plane to allow conjugation with the carboxylate. This contrasts with the η^3 mode found for NHC−CO_2 when cod dissociates.

The transition state for C−C cleavage, **Rh-cod-OCTS**, has been located on the potential energy surface (Figure 8) 25.5 kcal mol^{-1} above **Rh-cod-OO** (Figure 9). At the transition state, the Rh−C2 and Rh−O bonds are almost fully formed (2.220 and 2.102 Å, respectively) and the C−C bond is significantly elongated (1.845 Å). All attempts to locate a minimum in which the CO bond of the carboxylate group is coordinated to Rh prior to C−C bond cleavage, as found in the case of **Rh−Cl**, failed. Thus **Rh-cod-OCTS** leads directly to the product of reaction, **Rh-cod-prod**, 6 kcal mol^{-1} above **Rh-cod-OO**, having an η^1-O coordinated CO_2. Substitution of the labile CO_2 ligand by Cl^- produces the desired Rh(cod)Cl(NHC) **4**.

Discussion

Phosphines readily form complexes because they have a kinetically available lone pair. In contrast, N,N′-disubstituted imidazolium salts, typical precursors of NHCs, need to be deprotonated first. The resulting free NHC has a free lone pair and often readily binds to a metal, but it is itself a strong base. A strong base is not always compatible with the presence of a

sensitive functionality on the NHC or with certain metal salts or complexes required for specific applications.

To solve this problem, we have used NHC carboxylates, NHC−CO_2, neutral, isolable reagents, capable of transferring the NHC to a variety of metal centers to give complexes with a variety of ligand to metal ratios depending on the exact conditions. We have adapted a known synthesis of N,N′-dimethyl NHC carboxylates where no base is needed, using dimethyl carbonate (DMC) as the alkylating and carboxylating agent. This converts a N-substituted imidazole into the N,N′-disubstituted NHC carboxylates avoiding the high CO_2 pressures and strong base conditions required in the traditional synthesis of NHC carboxylates from imidazolium salts.

A limitation of the DMC route is that it cannot so far be extended to other dialkyl carbonates and so at least one N-substituent of the NHC has to be methyl. To help resolve this problem, we have shown that the most widely used NHC, N,N′-dimesityl NHC or IMes, can be introduced using the corresponding ester, NHC−COO^iBu. This ester is formed from the imidazolium salt with base and isobutyl chloroformate. The ester reacts more slowly with typical metal precursors than does NHC−CO_2, perhaps because the ester has to hydrolyze with adventitious water to give the NHC−CO_2 form before NHC transfer can occur.

Mechanism of Formation of NHC−CO_2. For the purely organic alkylation/carboxylation of N-methyl imidazole by DMC, the calculations show an endothermicity of 9.4 kcal mol^{-1}, not accounting for the interaction between NHC−CO_2 and methanol, but precipitation of the product is expected to drive the reaction. The overall potential energy surface for the calculated path, shown in Figure 3, has just one significant barrier associated with the S_N2 methyl transfer from DMC to the imidazole nitrogen. The barrier is consistent with the need to heat the reaction mixture. The overall transformation does not contain any unusual chemical step other than the formation of the CC bond between the NHC and CO_2, which normally requires a high CO_2 pressure,[26] but this is not needed here. This may be because the formation of **Prod$_2$** creates both the NHC and the CO_2 at the same time and in close proximity, favoring rapid formation of the NHC carboxylate via the low-energy barrier nucleophilic attack on CO_2 by the NHC. Even passage of N_2 through the reaction mixture only slightly decreases the yield of NHC−CO_2.

The fact that the S_N2 step is rate-determining explains why the reaction was not possible with any other carbonate than DMC. Diethyl carbonate, for example, would be expected to have a higher barrier S_N2 step, leading to a higher reaction temperature. The higher S_N2 barrier for the ethyl carbonate is supported by the general observation that steric effects strongly retard such reactions[31] and computationally for the present system by a 2.7 kcal mol^{-1} increase in the barrier height on moving to ethyl from methyl. Beyond 90 °C, however, the 2-carboxylate converts to the 4-carboxylate, so the desired 2-isomer cannot be obtained at the higher temperature required for diethyl carbonate.

Alternate NHC Transfer Pathways: Partial Decoordination of cod versus Loss of Cl^-. Moving to the transfer of the NHC to the metal, [Rh(cod)Cl] monomer has been taken as the relevant form, consistent with the kinetics showing dissociation of the dimer. Two alternate pathways must be considered, having the potential energy profiles shown in Figures 7 and 9. In either case, the reaction requires the presence of two *cis* empty coordination sites on the metal. Despite all attempts, no pathway in which only a single coordination on the metal was available could be identified, implying the absence of an associative pathway that might normally have been thought likely for a d^8 square planar metal. To create these empty sites, we invoke partial decoordination of cod or, alternatively, loss of Cl^-. The decoordination of cod, which leads to an η^2-cod (i.e., bound to the metal only via one of the two double bonds), has a rather high-energy barrier (around 45 kcal mol^{-1}). After coordination of NHC−CO_2, the individual steps leading to the desired final product have significantly lower barriers. The coordination mode of NHC−CO_2 in the case of partially coordinated cod is highly unusual. The expected κ^2-coordination mode, bound via lone pairs on each of the two O atoms, is perhaps prevented by the steric effect of the nearby dangling HC═CH group of the η^2-cod.

The NHC−CO_2 ligand is coordinated in an η^3-allylic manner, but in two possible ways depending on the degree of advancement along the pathway. The first way involves the O−C−O group, which leaves the C2 carbon of NHC uncoordinated. The second way involves the O−C−C group, which leaves the remaining carboxylate oxygen uncoordinated. These two coordination modes are energetically relatively close because of the conjugation between the CO_2 and NHC fragments, which adds electron density at C2 of NHC. The cleavage of the CC bond occurs with a relatively low-energy barrier ($\Delta E^{\ddagger} = 6.9$ kcal mol^{-1}) because the associated formation of CO_2 drives the energy down.

The pathway via chloride dissociation is only feasible in a highly polar solvent, such as the MeCN used experimentally. Modeling the real solvent by the continuum method, with single-point calculations on gas-phase optimized geometries, underestimates the stabilizing effect of the solvent especially because the minima and transition states were not reoptimized with the continuum model. Despite this, the loss of chloride is found to be energetically very easy. The NHC−CO_2 coordinates in the usual κ^2 form because η^4-cod does not approach the N-methyl substituent of the NHC group. The energy barrier for CC cleavage is calculated to be rather high (ca. 25 kcal mol^{-1}). To reach this transition state, one needs to bend the NHC−CO_2 group to move it out of the plane and approach a geometry similar to the η^3-form discussed above. Since we start from a more stable coordination mode, this costs more than by using the cod decoordination path. Even with this requirement, the highest point on the potential energy surface is lower than the transition state for cod dissociation. Provided that the solvent is sufficiently polar, this path should be favored. Indeed, the strongly inhibiting effect of excess chloride ion on the NHC transfer rate is entirely consistent with the chloride dissociation pathway being followed in the experimental system.

Two vacant sites are required for NHC transfer. We propose that only the low barrier chloride dissociation path can occur in the absence of heating. This generates two sites from the [Rh(cod)Cl] monomer and [M(cod)(NHC)Cl] is formed in Table 1 entries 1 and 2. The second NHC cannot be transferred because two sites are no longer available. Likewise, at room

(31) Caldwell, D.; Magnera, T. F.; Kebarle, P. *J. Am. Chem. Soc.* **1984**, *106*, 959−966.

temperature, only one PPh_3 or one pyridine is substituted in $[M(cod)L_2]^+$ (L = PPh_3 or pyridine; Table 1 entries 4b and 5b) because once $[M(cod)(NHC)L]^+$ is formed, only one site is available by dissociation of the second L and not two sites as in $[M(cod)L_2]^+$, so the second NHC transfer cannot occur. On heating to 75 °C with the second equivalent of NHC−CO_2, the second pathway, cod dissociation to the η^2 form can now occur as well as dissociation of L, creating two sites and allowing the second NHC transfer. This explains the formation of $[M(cod)(NHC)_2]^+$ in Table 1 (entries 4a and 5a). In the Pd(II) cases of Table 1, entries 6 and 7, the tris-NHC is formed even though models show no particular steric problem in the hypothetical tetrakis-NHC species. This fits the two-site reactivity model in that successive NHC transfers occur until, in the $[Pd(NHC)_3X]^+$ species, only one site can be created by dissociation of X (= OAc or Cl), so the reaction goes no further. The Pt(II) case of entry 8 follows exactly the same logic. The Ru(II) case, where only one NHC is transferred, may be the result of dissociation of a *single* Cl from the $[(ArH)RuCl_2]$ monomer alone being permitted. This would be explained on the plausible basis that a second Cl dissociation from a cationic $[(ArH)RuCl]^+$ monomer is harder than the first. In the case of $IrCl(CO)(PPh_3)_2$ (entry 9), only one NHC is transferred to give *trans*-$[Ir(CO)(NHC)(PPh_3)_2]Cl$. If a chloride and a PPh_3 can dissociate, the first transfer is consistent with the two-site model. Subsequent dissociation of the two mutually trans PPh_3 ligands can only give trans vacant sites, but the two-site model requires cis sites to be created. The second NHC is therefore not transferred.

Conclusion

N,N′-Disubstituted imidazolium carboxylates, readily available, isolable, air- and water-stable reagents, efficiently transfer NHC groups to Rh, Ir, Ru, Pt, and Pd, to give novel NHC complexes. The NHC esters are also effective. A net N to C rearrangement of an N-alkyl imidazole rhodium complex to the corresponding NHC complex was also possible with DMC. DFT calculations identify the steps needed to form the carboxylate from imidazole and $(MeO)_2CO$ (DMC): an S_N2 methyl transfer from DMC to imidazole, followed by a proton transfer from the imidazolium CH to the carboxylate counterion, produce the free NHC H-bonded to a methanol molecule with a weakly bonded CO_2. The nucleophilic NHC attacks CO_2 to form NHC−CO_2. NHC transfer to the metal with loss of CO_2 has been calculated for Rh(cod)Cl. A proposed two-*cis*-site reactivity model rationalizes the experimental data: two such vacant sites at the metal are needed to allow coordination of the NHC−CO_2 carboxylate and subsequent CC cleavage with NHC transfer. Partial decoordination of cod or loss of chloride is thus required for Rh(cod)Cl. Chloride dissociation, calculated to be easier in a polar solvent, is confirmed experimentally from the retarding effect of excess chloride ion. This chemistry provides an alternative route to NHC complexes that may prove widely useful.

Experimental Section

General Methods. All starting materials and reagents were obtained from commercial sources and used as received unless otherwise noted. All reactions were performed under an argon atmosphere using standard Schlenk techniques, and acetonitrile was distilled over calcium hydride. All glassware was dried overnight prior to use. ^1H, ^{13}C, and ^{31}P NMR spectra were obtained using a Bruker spectrometer operating at 400 MHz. Chemical shifts are reported in ppm with the residual solvent as an internal reference. Compounds **1** and **3**[18] were synthesized by previously described methods. Di-μ-chlorobis(*p*-cymene)chlororuthenium(II) was obtained from Strem Chemicals (Newburyport, MA 01950 USA) and was used as received.

Kinetic Studies. Rate Order with Respect to $[Rh(cod)Cl]_2$. Trimethoxybenzene (0.0100 g, 6.0×10^{-5} mol) and $[Rh(cod)Cl]_2$ (0.0082 g, 1.66×10^{-5} mol) were added to an airtight NMR tube which was purged with nitrogen. A 1.0 mL aliquot of d_3-acetonitrile was added, and a $t = 0$ NMR spectrum was taken to measure the relative concentrations of the Rh dimer (4.12 ppm, 4H) to the internal standard (6.05 ppm, 3H). This was found to be 0.2798, after correcting for the number of protons. The temperature of the sample was recorded to be 22.5 °C. Under a nitrogen flow 0.060 g of 1-methyl,3-butyl imidazolium carboxylate (**24**) (3.32×10^{-4}mol, 10× excess given the 2:1 stoichiometric ratio of the reactants) was added quickly, and spectra were immediately taken at the set times and the relative concentration of the Rh dimer to the internal standard was recorded.

Rate Order with Respect to NHC−CO_2. Trimethoxybenzene (0.0100 g, 6.0×10^{-5} mol), $[Rh(cod)Cl]_2$ (0.0843 g, 1.71×10^{-4}mol, 6× excess) and 1-methyl-3-butyl imidazolium carboxylate (**24**) (0.0052 g, 2.85×10^{-5}mol) were added to an airtight NMR tube which was purged with nitrogen. A 1.0 mL aliquot of d_3-acetonitrile was added. The temperature of the sample was recorded to be 28.3 °C. NMR spectra were immediately taken at the set times, and the relative concentration of the carboxylate (7.28 ppm, 2H) to the internal standard (6.05 ppm, 3H) was recorded and corrected for the number of protons.

***N,N′*-Dimethylimidazolium-2-carboxylate (2).** This known compound was prepared by a modification of the previously reported[24] procedure. A screw-top pressure tube (Fischer) was charged with dimethyl carbonate (3.0 mL), 1-methylimidazole (2 mL), and a stir bar. It was sealed and heated for 30 h at 90 °C. After approximately 2 h, the initially clear solution became cloudy with white precipitate, and after 24 h there was a copious amount of the white solid in a brown supernatant liquid. The solid was filtered and was washed thoroughly with methylene chloride (3 × 15 mL), acetone (3 × 15 mL), and ether (2 × 10 mL). The white solid proved to be the 2-carboxylate with less than 3% of the 4-carboxylate isomer. The solid was isolated with a total yield of 2.80 g (82%) and characterized by ^1H NMR (500 MHz, D_2O) δ 3.82 (s, 6H, *N*-CH_3), 7.26 (s, 2H, H-4 and H-5). $^{13}C\{^1H\}$ NMR (100 MHz, D_2O) δ 36.58, 121.89, 139.25, 157.56. The spectral data are consistent with literature data.[24] If the reaction is carried out above 100 °C the ratio of 4-carboxylate to 2-carboxylate is greatly increased. The mixed 2- and 4-isomeric material can be used directly for transfer to a transition metal, because only the 2-isomer undergoes transfer.

***N,N′*-Dimethylimidazolium-4-carboxylate.** This known[26] compound was synthesized according to the same method used above for the 2-carboxylate but at 120 °C for 30 h. The white precipitate so formed was filtered and washed as described above to give a yield of the 4-isomer of 3.06 g (92%). ^1H NMR (500 MHz, D_2O) δ 3.75 (s, 3H, *N1*−CH_3), 3.82 (s, 3H, *N3*−CH_3), 7.64 (s, 1H, H-5); ^{13}C NMR (D_2O, 125 MHz): δ 35.50, 36.41, 127.0, 130.51, 137.82, 163.13. The identification of the 4-carboxylate was confirmed by comparison to the literature NMR spectra.[26]

Chloro(η^4-1,5-cyclooctadiene)(1,3-dimethylimidazole-2-ylidene)-rhodium(I) (4). This known[28] compound was prepared from a mixture of $[Rh(cod)Cl]_2$ (500 mg, 1.01 mmol) and *N,N′*-dimethyl imidazolium carboxylate (**2**) (340 mg, 2.41 mmol) by stirring in acetonitrile (7 mL) for 40 min at room temperature in a Schlenk flask. Alternatively, this compound can be prepared by heating the same mixture to 75 °C for 15 min. In either case, the reaction mixture was dried *in vacuo* and washed three times with diethyl ether. The yellow solid obtained was analytically pure (638 mg, 93%). ^1H NMR (400 MHz, $CDCl_3$) δ 6.72 (s, 2H, NCH), 4.94 (m, 2H, cod CH), 4.02 (s, 6H, CH_3), 3.22 (m, 2H, cod CH), 2.34 (m, 4H, cod CH_2), 1.88 (m, 4H, cod CH_2). $^{13}C\{^1H\}$

NMR (100 MHz, $CDCl_3$) δ 182.84 (d,[1] $J_{Rh-C} = 50.9$ Hz, NCN), 122.04 (NCH), 98.72 (d, $^1J_{Rh-C} = 6.9$ Hz, cod CH), 67.84 (d,[1] $J_{Rh-C} = 14.6$ Hz, cod CH), 37.81 (CH_3), 33.13 (d, $^1J_{Rh-C} = 1.0$ Hz, cod CH_2), 29.05 (cod CH_2). These NMR data are consistent with those reported in the literature.[28]

Chloro(η^4-1,5-cyclooctadiene)(1,3-dimethylimidazole-2-ylidene)-iridium(I) (7). This known[28] compound was synthesized following the above procedure but with $[Ir(cod)Cl]_2$ (60 mg, 89.2 μmol) and *N*,*N*′-dimethyl imidazolium carboxylate (**2**) (30 mg, 212 μmol) in MeCN (5 mL). After 20 min of heating (oil bath, 75 °C) the color of the solution changed from red to orange. The reaction mixture was cooled, and the solvent was removed *in vacuo*. The solid was dissolved in 2 mL of methylene chloride and was purified by column chromatography by elution with 1:1 hexane/ethyl acetate. The product was obtained by dissolving the solid in dichloromethane and recrystallizing by addition of ether to yield an orange microcrystalline solid (63 mg, 82%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.97 (s, 2H, NCH), 4.35 (m, 2H cod CH), 3.89 (s, 6H, CH_3), 2.99 (m, 2H, cod CH), 2.20 (m, 4H, cod CH_2), 1.60−1.73 (m, 4H, cod CH_2). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 176.60 (s, NCN), 122.80 (s, NCH), 83.64, 53.28, 31.02, 31.75 (s, cod), 37.25 (NCH_3). These NMR spectra are consistent with literature data.[27] The literature ^{1}H NMR shifts for the cod ligand in $CDCl_3$ solution were reported as δ: 5.23, 4.2, 1.89, 1.50. However in our hands we found different values, reported above. All other spectroscopic data for this compound are in agreement with the published data.[28]

Dichloro(1,3-dimethylimidazole-2-ylidene)(*p*-cymene)ruthenium-(II) (9). This known[28] compound was prepared as follows. A dry Schlenk tube was charged with di-μ-chlorobis[*p*-cymene)chlororuthenium(II) (**8**) (60 mg, 98.3 μmol) and **2** (29 mg, 210 μmol) which were dissolved in 4 mL of acetonitrile. The reaction was stirred for 10 min at room temperature and then heated in an oil bath at 75 °C for 2 h. It was allowed to cool, and excess **2** was filtered from the reaction mixture. The filtrate was then concentrated to dryness *in vacuo* and recrystallized from 1:3 CH_2Cl_2/ether to afford compound **9** as orange-red needles (66 mg, 85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.97 (s, 2H, NCH), 5.41 (d, $^3J = 5.8$ Hz, 2H), 5.13 (d, $^3J = 5.8$ Hz, 2H), 2.68 (sept, $^3J = 6.8$ Hz, 1H), 2.02 (s, 3H, methyl) 3.96 (s, 6H, CH_3), 1.22 (d, $^3J = 6.8$ Hz, 6H, methyl). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ : 173.14, 123.68, 84.68, 82.20, 39.51, 30.78, 22.46, 18.62. These NMR data are consistent with the literature.[28]

(η^4-1,5-Cyclooctadiene)(bis-1,3-dimethylimidazole-2-ylidene)iridium(I) Hexafluorophosphate (11). This compound was prepared from $[Ir(cod)(PPh_3)_2]PF_6$ (**10**) (114 mg, 117.5 μmol) and **2** (41 mg, 293.8 μmol) dissolved in acetonitrile (4 mL) in a 10-mL Schlenk flask. The reaction mixture was stirred for 10 min at room temperature and was then heated in an oil bath (75 °C, 2 h), during which it turned to a bright orange. It was then allowed to cool, and the solution was filtered to remove excess imidazolium carboxylate, after which the solution was concentrated to dryness *in vacuo*. The solid was dissolved in 2 mL of methylene chloride and was purified by column chromatography by elution with 4:1 hexane/ethyl acetate. A bright orange fraction was eluted with a solution of KPF_6 (1 equiv) in acetone. Crystallization of this fraction from 1:3 CH_2Cl_2/diethyl ether yielded compound **11** as orange prisms (64 mg, 84%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.10 (s, 4H, NCH), 3.89 (s, 6H, CH_3), 3.72 (br m, 4H, cod CH), 2.10 (br m, 4H, cod CH_2), 1.89 (br m, 4H, cod CH_2). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ: 178.88 (s, NCN), 124.70 (s, NCH), 77.22, 39.22 (s, cod) 35.87 (s, NCH_3). ^{31}P NMR (162 MHz, $CDCl_3$) δ: −143.12 (PF_6). Analysis calculated for $C_{20}H_{36}F_6IrN_4P_2$: C, 33.91%; H, 4.43%; N, 8.79%. Found: C, 34.06%; H, 4.53%, N, 8.84%. Complex **11** was also made by an analogous procedure using $[Ir(cod)(py)_2]PF_6$ rather than $[Ir(cod)(PPh_3)_2]PF_6$ to obtain a yield of 58 mg, 76%. In both cases the identity of the products was confirmed by NMR spectroscopic comparison with our own authentic materials.

(η^4-1,5-Cyclooctadiene)(1,3-dimethylimidazole-2-ylidene)(triphenylphosphine)iridium(I) Hexafluorophosphate (12). This known[4] compound was prepared as follows. $[Ir(PPh_3)_2(cod)]PF_6$ (144.5 mg, 149 μmol) and **2** (21 mg, 149 μmol) were dissolved in acetonitrile (10 mL) in a 25-mL Schlenk flask. This reaction mixture was stirred for 2 h at room temperature, after which it was filtered and concentrated to dryness *in vacuo*. The solid was dissolved in 2 mL of methylene chloride and was purified by column chromatography by elution with 1:1 hexane/ethyl acetate followed by elution of a bright yellow fraction with a solution of KPF_6 (1 equiv) in acetone, which afforded the bright yellow product as the hexafluorophosphate salt. Crystallization of this fraction from 1:4 acetone/diethyl ether yielded compound **12** as orange needles (106 mg, 89%). ^{1}H NMR (400 MHz, d^6-$CDCl_3$) δ: 7.05−7.51 (m, 15H, Ar), 6.91 (s, 2H, NCH), 4.21 (b s, 2H, cod CH), 3.70 (b s, 2H, cod CH), 3.49 (s, 6H, CH_3), 2.42 (br m, 4H, COD CH_2), 2.05 (br m, 4H, cod CH_2). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 174.86, 132.13, 133.20, 131.96, 130.05, 129.72, 129.23, 128.81, 124.14, 86.22, 86.02, 80.45, 37.11, 31.26, 30.10. ^{31}P NMR (121 MHz, CD_2Cl_2) δ: 18.29 (PPh_3), −144.41 (PF_6). ESI-MS (*m*/*z*) M^+ calcd for $C_{31}H_{35}N_2PIr$, 659.2; found, 659.7. These NMR data are consistent with those reported in the literature.[4]

(η^4-1,5-Cyclooctadiene)(1,3-dimethylimidazole-2-ylidene)(pyridine)iridium(I) Hexafluorophosphate (13). This known[4] compound was prepared from $[Ir(py)_2(cod)]PF_6$ (90 mg, 149 μmol) and **2** (21 mg, 149 μmol) dissolved in acetonitrile (10 mL) in a 25-mL Schlenk flask. The reaction mixture was stirred for 2 h at room temperature, after which it was concentrated to dryness *in vacuo*. The solid was dissolved in 2 mL of methylene chloride and was purified by column chromatography by elution with 1:1 hexane/ethyl acetate followed by elution of a bright yellow fraction with a solution of KPF_6 (1 equiv) in acetone, which afforded the bright yellow product as the hexafluorophosphate salt. Crystallization of this fraction from 1:4 acetone/diethyl ether yielded compound **13** as yellow needles (72 mg, 78%). ^{1}H NMR (400 MHz, d^6-acetone) δ: 8.97 (d, 2H, pyridine), 7.98 (t, 1H, pyridine), 7.66 (dd, 2H, pyridine), 7.24 (s, 2H, NCH), 4.18 (s, 6H, CH_3), 4.09 (br m, 2H, cod CH), 3.79 (br m, 2H, cod CH), 2.44 (br m, 4H, cod CH_2), 1.97 (br m, 4H, cod CH_2). ^{13}C {^{1}H} NMR (100 MHz, d^6-acetone) δ: 172.25, 151.70, 139,31, 127.65, 123.90, 83.87, 64.01, 37.50 (s, COD) 32.75, 30.21 (s, NCH_3). ^{31}P NMR (162 MHz, d^6-acetone) δ: −143.12 (PF_6). ESI-MS (*m*/*z*) M^+ calculated for $C_{18}H_{25}IrN_3$, 476.17; found, 476.87. Anal. calcd for $C_{18}H_{25}F_6IrN_3P$: C, 34.84%; H, 4.06%; N, 6.77%. Found: C, 34.80%, H, 4.01%, N, 6.65%.

Acetato(tris-1,3-dimethylimidazole-2-ylidene)palladium(II) Acetate (14). A 10-mL Schlenk flask was charged with $Pd(OAc)_2$ (109 mg, 486.6 μmol) and **2** (274 mg, 1.94 mmol). Acetonitrile (7 mL) was added under an inert atmosphere, and the reaction mixture was heated in a 75 °C oil bath for 12 h. The solution turned yellow and then pale yellow during the course of the reaction. It was then cooled and filtered through Celite, after which the filtrate was concentrated to dryness *in vacuo* and washed with ether (2 × 10 mL). The product was recrystallized twice from 1:3 CH_2Cl_2/diethyl ether to yield light yellow prisms of **14** (177 mg, 71%). ^{1}H NMR (400 MHz, d^6-DMSO) δ: 7.37 (s, 2H, central NCH), 7.30 (s, 4H, wing NCH), 3.73 (s, 12H, wing CH_3), 3.55 (s, 6H, central CH_3), 3.20 (br s, 6H, H_2O) 1.60 (s, 3H, O_2CCH_3, bound) 1.49 (s, 3H, O_2CCH_3, unbound). ^{13}C {^{1}H} NMR (100 MHz, d^6-DMSO) δ: 175.64 (s, NCN), 174.69 (s, NCN), 122.45 (s, NCH), 122.16 (s, NCH′), 36.92 (s, NCH_3), 36.70 (s, NCH_3′), 34.13 (s, OAc), 22.88 (s, OAc′). Anal. calcd for for $C_{19}H_{33}N_6O_4Pd\cdot3.5H_2O$: C, 39.43%; H, 6.97%; N, 14.51%. Found: C, 39.26%; H, 6.36%; N, 14.51%.

Chloro(tris-1,3-dimethylimidazole-2-ylidene)palladium(II) Chloride (15). A 10-mL Schlenk flask was charged with $PdCl_2(MeCN)_2$ (100 mg, 389 μmol) and **2** (220 mg, 1.55 mmol). Acetonitrile (5 mL) was added under an inert atmosphere, and the reaction mixture was heated in a 75 °C oil bath for 12 h. The solution was then cooled and filtered through Celite, after which the filtrate was concentrated to dryness *in vacuo* and washed with ether (2 × 10 mL). The product was recrystallized twice from 1:3 CH_2Cl_2/diethyl ether to yield yellow

prisms of **15** (117 mg, 65%). ^{1}H NMR (400 MHz, d^6-DMSO) δ: 7.34 (s, 2H, central NCH), 7.21 (s, 4H, wing NCH), 3.84 (s, 12H, wing CH_3), 3.42 (s, 6H, central CH_3). ^{13}C {^{1}H} NMR (100 MHz, d^6-DMSO) δ: 176.51 (s, NCN), 172.12 (s, NCN), 142.52 (s, NCH), 122.10 (s, NCH′), 34.45 (s, NCH_3), 32.21 (s, NCH_3′). The identity of the products was confirmed by NMR spectroscopic comparison with authentic material.

Chloro(tris-1,3-dimethylimidazole-2-ylidene)platinum(II) Chloride (16). A 10-mL Schlenk flask was charged with K_2PtCl_6 (109 mg, 486.6 μmol) and **2** (274 mg, 1.94 mmol). Acetonitrile (8 mL) was added under an inert atmosphere, and the reaction mixture was heated in a 75 °C oil bath for 24 h. The solution was cooled and filtered through Celite, after which the filtrate was evaporated to dryness *in vacuo* and washed with ether (2 × 10 mL). The product was recrystallized first from 1:3 acetone/diethyl ether and a second time from 1:3:2 CH_2Cl_2/diethyl ether/pentane to yield light yellow prisms of **12** (177 mg, 71%). ^{1}H NMR (400 MHz, CD_3CN) δ: 7.21 (s, 2H, central NCH), 7.12 (s, 4H, wing NCH), 3.73 (s, 12H, wing CH_3), 3.55 (s, 6H, central CH_3). ^{13}C {^{1}H} NMR (100 MHz, d^6-CD_3CN) δ: 146.35 (s, NCN), 145.56 (s, NCN), 121.26 (s, NCH), 120.89 (s, NCH′), 36.82 (s, NCH_3), 35.54 (s, NCH_3′). Anal. calcd for $C_{15}H_{24}Cl_2N_6Pt$: C, 32.50%; H, 4.36%; N, 15.16%. Found: C, 32.61%; H, 4.30%, N, 15.28%. ESI-MS (*m*/*e*) calcd: for $[Pt(NHC)_3Cl)]^+$, 518.91; found, 519.85.

***trans*-Bis(triphenylphosphine)(carbonyl)(1,3-dimethylimidazole-2-ylidene)iridium(I) Chloride (17).** This new compound was prepared from $Ir(PPh_3)_2(CO)Cl$ (100 mg, 128 μmol) and **2** (36 mg, 256 μmol) in acetonitrile (5 mL) in a 10-mL Schlenk flask. The mixture was stirred for 6 h at room temperature, after which it was filtered and the filtrate was concentrated to dryness *in vacuo*. Crystallization of this fraction from 1:4 dichloromethane/diethyl ether yielded the product as yellow prisms (88 mg, 79%). ^{1}H NMR (400 MHz, CD_2Cl_2) δ: 7.56−7.47 (m, 30H, PPh_3), 6.46 (s, 2H, CNH), 2.91 (s, 6H, wing CH_3). ^{13}C {^{1}H} NMR (100 MHz, CD_2Cl_2) δ: 184.36, 175.26, 133.48, 133.43, 131.93, 131.56, 128.55, 36.27. ^{31}P NMR (161 MHz, CD_2Cl_2) δ: 20.68. ESI-MS (*m*/*e*) calculated: for $[Ir(NHC)(PPh_3)_2(CO)]^+$, 841.21; found, 841.72. Analysis calculated for $C_{42}H_{38}ClN_2OP_2Ir$: C, 57.56%; H, 4.37%; N, 3.20%. Found: C, 57.42%; H, 4.31%, N, 3.35%.

Chloro(η^4-1,5-cyclooctadiene)(1-butyl-3-methylimidazole-2-ylidene)-rhodium(I). This known[32] compound was prepared from a mixture of bis(η^4-1,5-cyclooctadiene)(di-μ-chloro)dirhodium (500 mg, 1.01 mmol) and *N*-methyl-*N*′-*n*-butylimidazolium-2-carboxylate (404 mg, 2.2 mmol) stirred in acetonitrile (10 mL) for 40 min at room temperature in a Schlenk flask. The reaction mixture was dried *in vacuo* and washed with diethyl ether (3 × 10 mL). The yellow solid was dissolved in methylene chloride (2 mL) and purified by column chromatography via elution with 1:1 (v/v) hexanes/ethyl acetate or, better, can alternatively be recrystallized from methylene chloride/diethyl ether to give small yellow prisms (693 mg, 90%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.78 (d, J = 1.8 Hz, 2H), 4.99 (br m, 2H, COD CH), 4.46 (t, 2H, J = 7.8 Hz), 4.02 (s, 3H, CH_3), 3.30 (br m, 1H, COD CH), 3.23 (br m, 1H, COD CH), 2.34 (m, 4H, COD CH_2), 1.92 (br m 4H COD CH_2 and 2H Bu CH_2), 1.48 (m, 2H), 1.01 (t, 3H, J = 7.4 Hz). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ: 13.71 (s), 28.75 (s), 32.68 (s), 33.05 (s), 37.62 (s), 50.23 (s), 67.78 (d, $^1J_{Rh-C}$ = 14.1 Hz), 98.26 (d, $^1J_{Rh-C}$ = 7.7 Hz), 120.13 (s), 121.99 (s), 181.43 (d, ^1J_C−Rh = 48.2 Hz). ESI-MS (*m*/*z*) calcd for $[Rh(NHC)(cod)]^+$, 385.09; found, 385.26. These data are consistent with those reported in the literature.[32]

(η^4-1,5-Cyclooctadiene)(bis-1,3-dimethylimidazole-2-ylidene)iridium(I) Acetate (18). A 10-mL Schlenk flask was charged with $[Ir(cod)Cl]_2$ (162 mg, 162 μmol), **2** (57 mg, 0.4 mmol), and sodium acetate (0.100 g). Acetonitrile (10 mL) was added under an inert atmosphere, and the mixture was heated to reflux for 2 h, over which time it turned to a bright orange color. The solution was cooled and filtered through Celite, and the filtrate was concentrated to dryness *in vacuo* and washed with ether (2 × 10 mL). The crude solid was found to be analytically pure without further purification. It was recrystallized from 1:4 CH_2Cl_2/diethyl ether to yield bright orange needles of **18** (157 mg, 88%). ^{1}H NMR (400 MHz, $CDCl_3$), see compound **11**. The compound was converted to the hexafluorophosphate salt, **11**, by chromatographic separation using acetone/KPF_6, and all characterization data were found to match those of the authentic material (compound **11**).

(η^4-1,5-Cyclooctadiene)(bis-1,3-dimethylimidazole-2-ylidene)-rhodium(I) Acetate (19). The known[33] complex **19** was also made by an analogous procedure using $[Rh(cod)Cl]_2$ rather than $[Ir(cod)Cl]_2$ to obtain a yield of 112 mg, 75%. ^{1}H NMR (400 MHz, $CDCl_3$): 6.96 (s, 4H, NCH), 4.05 (br m, 4H, cod CH) 3.85 (s, 12H, CH_3), 2.22 (br m, 8H, cod CH_2), 2.10 (s, 3H, OAc). The identity of the compound was confirmed by comparison (NMR) with literature data.[33]

(η^4-1,5-Cyclooctadiene)(bis-1-*n*-butyl-3-methylimidazole-2-ylidene)iridium(I) Hexafluorophosphate (21). A screw-top pressure tube (Fischer) was charged with dimethyl carbonate (3.0 mL), 1-*n*-butylimidazole (2 mL), $[Ir(cod)Cl]_2$ (150 mg), and 2 mL of acetonitrile. The tube was immersed in a 90 °C oil bath and allowed to stir for 12 h. It was then fitted with a condenser and further refluxed for 14 h. The reaction mixture was then allowed to cool and was treated with $NaPF_6$ (60 mg) for 5 min, and the solvent was removed *in vacuo*. The oil was thoroughly washed with diethyl ether (5 × 10 mL) and was recrystallized from methylene chloride/pentane (1:3) to afford red crystals of **21** (88%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.17 (d, 2H), 7.00 (d, 2H), 4.47 (m, 2H), 4.31 (m, 2H), 3.91 (d, 6H), 3.81(m, 4H), 3.69 (m, 1H), 3.63 (m. 1H), 2.17 (m, 4H), 1.82 (m, 4H), 1.60 (m, 2H), 1.36 (m, 4H), 0.95 (2, three diastereomers, 6H). ESI-MS (*m*/*z*) calcd for $[Ir(NHC)_2(cod)]^+$, 576.82; found, 576.24. Anal. calcd for $C_{24}H_{40}F_6IrN_4P$: C, 39.94%; H, 5.59%; N, 7.76%. Found: C, 39.71%; H, 5.73%; N, 7.82%.

Chloro(η^4-1,5-cyclooctadiene)(1,3-dimesitylimidazole-2-ylidene)-rhodium(I) (22). This known[3] compound was synthesized as follows. A 25 mL round-bottom flask was charged with *N*,*N*′-2,4,6-trimethylphenyl imidazolium chloride (100 mg, 294.1 μmol) and potassium *tert*-butoxide (16 mg, 378 μmol). The flask was then charged with dry acetonitrile (10 mL) and stirred in an ice bath for 5 min, after which isobutyl chloroformate (1.20 mL, 880 μmol) was added *dropwise* through a syringe over the course of 10 min. The reaction was allowed to stir in an ice bath under a strictly inert atmosphere for an additional hour and then at room temperature for 6 h. The reaction mixture was then filtered and dried *in vacuo* to give a light yellow oil, which was washed with ether three times. To the resulting oil 6 mL of acetone were added with 1 equiv of $NaPF_6$. The resulting precipitate was filtered, and the filtrate was dried in vacuo. The white solid obtained was again washed with ether to give 59 mg, 78% of **11**. ^{1}H NMR (400 MHz, d^6-acetone) δ: 8.23 (s, 2H, NCCN), 7.08 (s, 4H, Ph), 3.77 (d, 2H, OCH_2), 2.21 (s, 6H, Me) 2.04 (s, 12H, Me), 1.41 (m, 1H, OCH_2CHMe_2), 0.44 (d, 6H, Me). ^{13}C {^{1}H} NMR (125 MHz, d^6-acetone) δ: 153.55, 142.79, 130.96, 126.46, 75.92, 21.49, 18.98, 17.77. $[Rh(cod)Cl]_2$ (57 mg, 114 μmol) was then added in MeCN (2 mL), and the reaction mixture was refluxed for 2 h. The solution was cooled, and the solvent was removed *in vacuo*. The resulting solid was redissolved in methylene chloride (2 mL) and subjected to column chromatography with 80/20 ethyl acetate/hexanes to afford a yellow solid after evaporation of solvent. It was recrystallized from methylene chloride/pentane (1:3) to afford pure product (0.49 g, 62%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.06 (s, 4H Mes), 6.99 (s, 2H NHC), 4.42 (s, 2H cod) 3.30 (s, 2H cod), 2.32 (s, 6H CH_3), 2.36 (s, 6H CH_3), 2.14 (s, 6H CH_3), 1.81 (m, 4H cod), 1.58 (m, 4H cod). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ: 18.5, 20.0, 21.4, 28.9, 33.2, 68.7 (d, $^1J_{Rh-C}$ = 14.3 Hz), 96.3 (d, $^1J_{Rh-C}$ =

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7.6 Hz), 124.3, 128.8, 129.8, 135.1, 137.0, 137.9, 139.2, 183.5 (d, $^1J_{Rh-C}$ = 52.5 Hz). These NMR data are consistent with those reported in the literature.[3]

Chloro(η^4-1,5-cyclooctadiene)(di-*n*-butylimidazole-2-ylidene)iridium(I). This known[34] compound was synthesized according to an analogous procedure to compound **22**, but using *N*,*N*′-di-*n*-butyl imidazolium bromide (76 mg, 294.1 μmol). The ester was used directly after its synthesis as above. [Ir(cod)Cl]$_2$ (77 mg, 114 μmol) was then added in MeCN (2 mL), and the reaction mixture was refluxed for 2 h, after which the compound was isolated by column chromatography with 80:20 hexanes/ethyl acetate and recrystallized in 4:1 CH_2Cl_2/ether to give orange needles (112 mg, 63%) identical to authentic material.

***N*-Methyl-*N*′-*n*-butylimidazolium-2-carboxylate (23).** This known,[26] asymmetrically substituted carboxylate was prepared by a modification of the procedure for **2**. A screw-top pressure tube (Fischer) was charged with dimethyl carbonate (3.0 mL), 1-*n*-butylimidazole (2 mL), and a stir bar. It was sealed and heated for 40 h at 95 °C. The solvent was then removed *in vacuo* to give a brown oil, which was washed with diethyl ether (3 × 15 mL). It was purified by recrystallization in acetonitrile to give a yellow solid, which was dried in vacuo to give the product (yield: 2.9 g, 78%). ^{1}H NMR (500 MHz, D_2O) δ 7.41 (d, 1H, ^3J = 1.8 Hz), 7.36 (d, 1H, ^3J = 1.8 Hz), 4.28 (t, 2H, *N*-CH_2−), 3.83 (s, N−Me), 1.58 (m, CH_2), 1.05 (m, CH_2), 0.70 (m, C−CH_3). ^{13}C{^{1}H} NMR (125 MHz, CD_3CN) δ 12.52 (s, C−CH_3), 18.99 (s, CH_2), 32.44 (s, CH_2) 35.19 (s, *N*-CH_3), 48.56 (s, *N*-CH_2−), 121.04 (s, C4), 121.91 (s, C5), 137.61 (s, C2), 160.12 (s, COO). This material was identified by comparison with the literature spectra.[26]

Computational Details. The calculations were performed with the Gaussian03 package[35] at the B3PW91 level.[36] Rhodium was represented by the relativistic effective core potential (RECP) from the Stuttgart group and the associated basis set,[37] augmented by an f polarization function (α = 1.350).[38] Chlorine was represented by the relativistic effective core potential (RECP) from the Stuttgart group and the associated basis set,[39] augmented by a d polarization function (α = 0.640).[40] A 6-31G(d,p) basis set was used for all the other atoms (C, N, H, O).[41]

The geometry optimizations were performed without any symmetry constraint followed by analytical frequency calculations to confirm that a minimum or a transition state had been reached. The nature of the species connected by a given transition state structure was checked by optimization as minima of slightly altered TS geometries along both directions of the transition state vector. The energies of all the systems studied at the B3PW91 level in the gas phase for the mechanism of NHC transfer to Rh were computed with inclusion of solvent effects (acetonitrile) according to the PCM scheme as implemented in Gaussian.[42] The geometries obtained in the gas phase were used without further reoptimization within the PCM methodology, and the united atom topological model with UAHF radii was used. It should be noted that although the reactions under studies are associated with a change of molecularity, we have used PCM energies *E* and not Gibbs energies *G* for characterizing the reaction paths. Computing the entropic contribution for these reactions, run in solution, by gas-phase modeling is most likely inadequate, in particular because no geometry optimization within the PCM scheme was performed. Due to the difficulties in calculating entropy in condensed phases, various alternatives have been suggested in the literature, including even the full neglect of the translational entropy, which is the greatest contribution to the total entropy changes.[43] Because of these limitations, we have considered only energies for the discussion but we provide Gibbs free energies in the Supporting Information for all species. In the cases where the gas-phase calculations could be used, we have verified that no change of mechanism results from the consideration of Gibbs free energies.

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Supporting Information Available: Complete reference for Gaussian 03 and DFT-computed Cartesian coordinates for the optimized molecules and their electronic *E* and Gibbs free energies *G* values. For the NHC transfer mechanism, PCM energy values are also given. This material is available free of charge via the Internet at http://pubs.acs.org.

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