

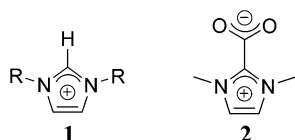
Disubstituted Imidazolium-2-Carboxylates as Efficient Precursors to N-Heterocyclic Carbene Complexes of Rh, Ru, Ir, and Pd

Adelina M. Voutchkova, Leah N. Appelhans, Anthony R. Chianese, and Robert H. Crabtree*

Chemistry Department, Yale University, 225 Prospect Street, New Haven, Connecticut 06520-8107

Received October 4, 2005; E-mail: robert.crabtree@yale.edu

While N-heterocyclic carbene (NHC) complexes have provided many of the most recent powerful homogeneous catalysts,¹ methods of synthesizing them have advanced more slowly. Two common routes are deprotonation of a precursor imidazolium salt (**1**), either by a strong base^{2a} or by a basic ligand,^{2b} and oxidative addition of the C–H bond of **1**.^{2c–d} The free carbene intermediate of the first route necessitates dry, air-free conditions and provides limited tolerance of other functionalities, while direct oxidative addition is known only for a number of specific cases. In an important advance, Lin et al. showed that Ag₂O can be used to form a Ag–NHC complex from the imidazolium salt which readily transfers the NHC to palladium and gold.³ Transmetalation to various metal species can also give a wide variety of NHCs of rhodium, copper, ruthenium, and iridium.^{4,5} Failures can still be encountered,⁶ however, and Ag-induced oxidative degradation of the imidazolium precursor has also been noted.⁷ Further methods⁸ are therefore eagerly sought.



We now report that *N,N'*-disubstituted imidazolium-2-carboxylates, air- and moisture-stable species, can transfer NHCs to a variety of metal salts with release of CO₂. For example, the *N,N'*-dimethyl imidazolium-2-carboxylate (**2**) reacts rapidly with [Rh(cod)Cl]₂ to produce Rh(cod)(NHC)Cl in 93% isolated yield (Scheme 1, cod = 1,5-cyclooctadiene) to give **3**. Carboxylate **2** also transfers the NHC to several other metal salts of Rh, Ir, Ru, and Pd (Table 1). Reactions of entries 1 and 2 are complete in as little as 20 min, while those of entries 3–6, in 2–12 h, to give mono-, bis-, or tris-NHC complexes in high yields. In addition to the cleavage of chloride-bridged dimers (Table 1, entries 1–3), displacement of neutral ligands such as triphenylphosphine (entry 4) and pyridine (entry 5) as well as anionic ligands such as acetate (entry 6) was also found. The reaction with Pd(OAc)₂ affords an unusual tris-NHC derivative in 71% yield (Figure 1).

This method affords products, such as **8** and **10**, which have not previously been synthesized. The remaining product complexes in Table 1 have previously been synthesized by the free carbene route⁹ or by oxidative addition of **1**,⁵ but the present method is considerably faster and affords comparable or better yields. This method does not require dry or air-free conditions for the NHC transfer, provided the substrate metal salt is not itself affected by air or water, as is the case for entries 2, 4, 5, and 6. The reaction in Scheme 1 was even carried out in 90:10 (v/v) H₂O–MeCN and afforded the same yield with no observable imidazolium salt. Conversion also even occurs at room temperature but, depending on the solvent, is limited by the low solubility of **2** under these conditions.

Scheme 1

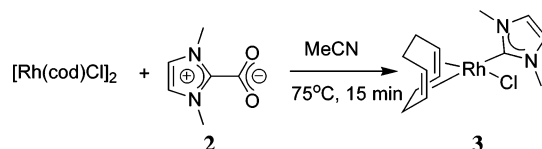


Table 1. NHC Metal Complexes Obtained from Reaction of Metal Salts with *N,N'*-Dimethyl Imidazolium Carboxylate (**2**)^{a,b}

entry	reactant	product	time (h)	yield % (lit.)
1	[Rh(cod)Cl] ₂	Rh(cod)(NHC)Cl (3)	0.3	93(91) ⁹
2	[Ir(cod)Cl] ₂	Ir(cod)(NHC)Cl (4)	0.3	82(90) ⁹
3	[(ArH)RuCl ₂] ₂ (5)	(ArH)RuCl ₂ (NHC) (6)	2	85(90) ⁹
4	[Ir(cod)(PPh ₃) ₂]PF ₆ (7)	[Ir(cod)(NHC) ₂]PF ₆ (8)	2	84
5	Ir(cod)(py) ₂]PF ₆ (9)	[Ir(cod)(NHC) ₂]PF ₆ (8)	2	76
6	Pd(OAc) ₂	[Pd(NHC) ₃ (OAc)]OAc (10)	12	71

^a Conditions: MeCN, 75 °C. ^b NHC = 1,3-dimethylimidazole-2-ylidene; cod = 1,5-cyclooctadiene; ArH = η^6 -*p*-cymene; py = pyridine.

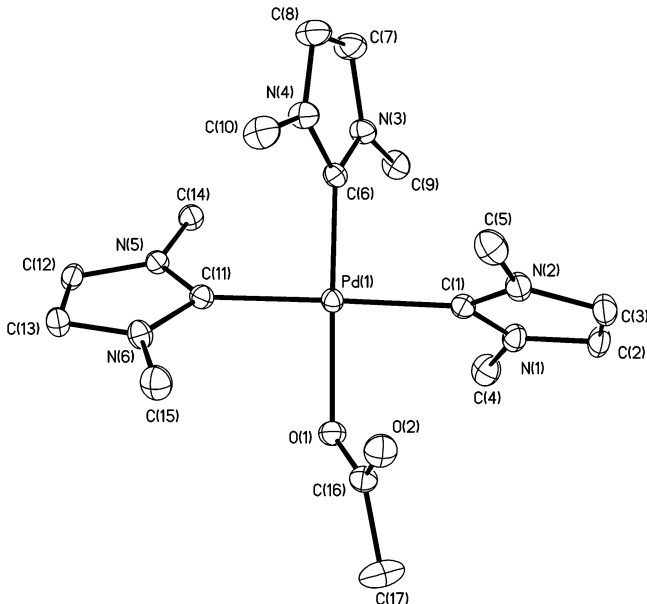
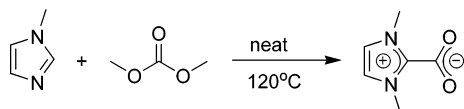


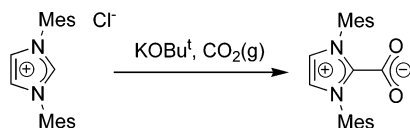
Figure 1. An ORTEP diagram of the cation of **10**. Selected bond lengths (Å) and angles (deg): Pd(1)–C(6), 1.968(3); Pd(1)–C(1), 2.036(3); Pd(1)–C(11), 2.049(3); Pd(1)–O(1), 2.096(2); C(6)–Pd(1)–C(1), 91.39(13); C(6)–Pd(1)–C(11), 89.72(13); C(1)–Pd(1)–C(11), 177.84(13); C(6)–Pd(1)–O(1), 175.81(11).

The utility of this procedure requires a generally applicable synthesis of the NHC carboxylates. The known¹⁰ synthesis of **2** by alkylation of methyl imidazole with (MeO)₂CO (Scheme 2) is of limited generality. Louie and co-workers¹¹ have reported a synthesis of the *N,N'*-di(mesityl)imidazolium-2-carboxylate using KOBu/CO₂ (Scheme 3).

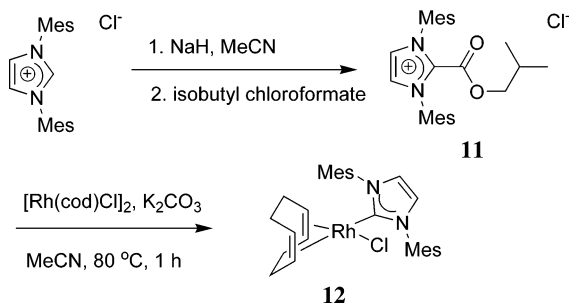
Scheme 2



Scheme 3



Scheme 4



In an alternate procedure, we now find that the new, easily synthesized imidazolium ester **11** is also capable of transferring the corresponding NHC (IMes) to Rh in 68% yield (Scheme 4). The imidazolium ester is prepared from IMes by deprotonation with NaH followed by treatment with isobutyl chloroformate. This allows extension of the method beyond the *N,N'*-dimethyl case.

Ester **11** provides a storable, convenient NHC transfer agent that requires less stringent conditions compared to the free NHC route. Since the transfer reactions described here are all insensitive to air and water, it seems unlikely that the free NHC is involved. Instead, an alternative process, such as coordination of the carboxylate via oxygen, followed by β -elimination, will need to be considered. Computational studies to resolve this point are in hand. In control experiments, we verified that reaction of the same metal precursors with imidazolium salt **1** under the conditions in Table 1 did not give any of the product obtained from **2**.

We have shown that *N,N'*-dialkylimidazolium-2-carboxylates offer a mild and highly efficient route to NHC complexes of rhodium, iridium, ruthenium, and palladium. The scope and

generality of this method remain to be investigated, as does the mechanism of carbene transfer. By avoiding the strong base needed in the free carbene route, our method minimizes possible side reactions. The oxidative degradation seen⁷ in the Ag₂O route should also be avoided. These conditions are some of the mildest thus far reported in the literature and offer hope for access to a new range of NHC metal complexes.

Acknowledgment. We would like to thank Dr. C. Incarvito for the crystallographic work and Prof. G. C. Micalizio for helpful discussions.

Supporting Information Available: Crystallographic data of **10** and experimental data are available (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) (a) Bourissou D.; Guerret, O.; Gabbai, F. P.; Bertrand, G. *Chem. Rev.* **2000**, *100*, 39–91. (b) Viciu, M. S.; Germaneau, R. F.; Nolan, S. P. *Org. Lett.* **2002**, *4*, 4053–4056. (c) Herrmann, W. A.; Köcher, C. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2163–2187. (d) Herrmann, W. A. *Angew. Chem., Int. Ed.* **2002**, *41*, 1290–1309. (e) Peris, E.; Crabtree, R. H. *Coord. Chem. Rev.* **2004**, *248*, 2239–2246. (f) Perry, M. C.; Burgess, K. *Tetrahedron: Asymmetry* **2003**, *14*, 951–961.
- (2) (a) Herrmann, W. A.; Kocher, C.; Goossen, L. J.; Artus, G. R. J. *Chem.—Eur. J.* **1996**, *2*, 1627–1636. (b) Öfele, K. *J. Organomet. Chem.* **1968**, *12*, P42–P43. (c) McGuinness, D. S.; Cavell, K. J.; Skelton, B. W.; White, A. H. *Organometallics* **1999**, *18*, 1596–1605. (d) Gründemann, S.; Albrecht, M.; Kovacevic, A.; Faller, J. W.; Crabtree, R. H. *J. Chem. Soc., Dalton Trans.* **2002**, 2163–2167.
- (3) (a) Wang, H. M. J.; Lin, I. J. B. *Organometallics* **1998**, *17*, 972–975. (b) Lin, I. J. B.; Vasam, C. S. *Comments Inorg. Chem.* **2004**, *25*, 75–129.
- (4) (a) Chianese, A. R.; Li, X. W.; Janzen, M. C.; Faller, J. W.; Crabtree, R. H. *Organometallics* **2003**, *22*, 1663–1667. (b) Coleman, K. S.; Chamberlayne, H. T.; Turberville, S.; Green, M. L. H.; Cowley, A. R. *Dalton Trans.* **2003**, 2917–2922.
- (5) (a) Viciano, M.; Mas-Marza, E.; Poyatos, M.; Sanau, M.; Crabtree, R. H.; Peris, E. *Angew. Chem., Int. Ed.* **2005**, *44*, 444–447. (b) Arnold, P. L.; Scarisbrick, A. C.; Blake, A. J.; Wilson, C. *Chem. Commun.* **2001**, 2340–2341. (c) Hu, X. L.; Castro-Rodriguez, I.; Olsen, K.; Meyer, K. *Organometallics* **2004**, *23*, 755–764.
- (6) Mata, J. A.; Chianese, A. R.; Miecznikowski, J. R.; Poyatos, M.; Peris, E.; Faller, J. W.; Crabtree, R. H. *Organometallics* **2004**, *23*, 1253–1263.
- (7) Chianese, A. R.; Zeglis, B. M.; Crabtree, R. H. *Chem. Commun.* **2004**, 2176–2177.
- (8) Yamaguchi, Y.; Kashiwabara, T.; Ogata, K.; Miura, Y.; Nakamura, Y.; Kobayashi, K.; Ito, T. *Chem. Commun.* **2004**, 2160–2161.
- (9) Herrmann, W. A.; Elison, M.; Fischer, J.; Koecher, C.; Artus, G. R. J. *Chem.—Eur. J.* **1996**, *2*, 772–780.
- (10) Holbrey, J. D.; Reichert, W. M.; Tkatchenko, I.; Bouajila, E.; Walter, O.; Tommasi, I.; Rogers, R. D. *Chem. Commun.* **2003**, 28–29.
- (11) Duong, H. A.; Tekavec, T. N.; Arif, A. M.; Louie, J. *Chem. Commun.* **2004**, 112.

JA056625K