COMMUNICATION

ChemComm
www.rsc.org/chemcomm

Catalytic olefin hydrogenation using N-heterocyclic carbene–phosphine complexes of iridium†

Leslie D. Vázquez-Serrano, Bridget T. Owens and Jillian M. Buriak*
Department of Chemistry, 1393 Brown Laboratories, Purdue University, West Lafayette, IN 47907-1393, USA. E-mail: buriak@purdue.edu; Fax: (765) 494-0239; Tel: (765) 496-3491

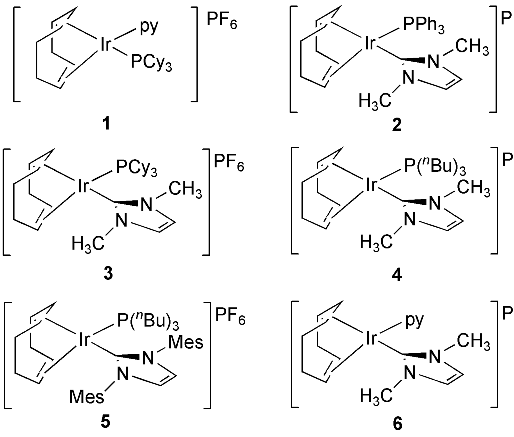
Received (in Purdue, IN, USA) 29th August 2002, Accepted 7th September 2002
First published as an Advance Article on the web 27th September 2002

N-heterocyclic carbene–phosphine complexes of iridium have been synthesized and examined for their performance in the catalytic homogeneous hydrogenation of a range of olefins; the reaction was further explored using para-hydrogen induced polarization (PHIP) ^{1}H NMR.

N-heterocyclic carbene (NHCs) complexes of late transition metals have been the focus of increasing interest due to the unique electronic properties of the carbenes,[1] their recent commercial availability,[2] and indications of increased stability of the metal complexes.[3] NHCs have shown promise as replacements for the commonly used, air sensitive phosphine-based class of ligands, but do have their own unique properties: they are strong σ donors, but are weak π-acceptors, and have an entirely different steric environment.[1,3a,4] A variety of metal complexes have been prepared in which one or more of the phosphine ligands have been replaced with NHCs; in many reported cases, this change results in an improvement of the catalytic properties and stability of the compounds under the reaction conditions.[1a,5] Because of the importance of catalytic olefin hydrogenation,[6] NHCs have been incorporated into known late transition metal ruthenium and iridium hydrogenation catalysts as phosphine substitutes.[1a,7] Much of the work has been inspired by the known high reactivity of Crabtree's catalyst,[8] **1**, but substitution of the tricyclohexyl phosphine ligand in **1** with NHCs leads to an active catalyst, but whose rate is reduced with respect to that of the parent compound.[7a] In this paper we describe the synthesis and testing of a new class of iridium(I) complexes which contain both a phosphine and a NHC ligand; in essence, the pyridine of **1** is replaced with a NHC. The complexes have similar reactivity as compared to **1** for hydrogenation of even hindered tertiary and quartenary olefins. With primary and secondary olefins, the reaction can be carried out with reagent grade solvents decanted in air. In addition, enhancements are observed in the para-hydrogen induced polarization (PHIP) ^{1}H NMR spectrum,[9] which suggest a dihydride mechanism.

Two different NHCs were examined in this study: 1,3-dimethylimidazol-2-ylidene (IMe) which is a rather unstable sterically unencumbered ligand,[1d] and 1,3-bis(2,4,6-trimethylphenyl)-imidazol-2-ylidene (IMes), a more stable, hindered variant. The complexes prepared from these two NHCs, compounds **2**–**6** (Scheme 1), are stable under ambient conditions in both the solid form (> 3 months) and in solution (1 week). Detailed procedures for the syntheses of the complexes are presented as ESI.† The most highly active complex of the NHC series, **4**, which contains the IMe ligand and tri(*n*-butyl)phosphine, was structurally characterized by X-ray crystallography (Fig. 1). As expected, the structure of the complex reveals a higher *trans* effect from the NHC compared to the alkyl phosphine, based upon the longer Ir–C bond lengths from the metal center to the COD ligand trans to the IMe carbon. Because of the high steric bulk of the IMes ligand, complexes containing this carbene could not be successfully prepared with bulky phosphines.

Complexes **1**–**6** were tested for the hydrogenation of the simple olefins shown in Scheme 1 and the results summarized in Table 1. Two major trends become obvious: first, complexes having a combination of a phosphine and a NHC (**2**–**5**) prove to be more effective than those with a combination of a pyridine and a NHC (complexes **6** and literature[7a]). The results indicate that the NHC ligands are more interesting for catalyst development than just simple phosphine substitutes. Indeed, substitution of just one of the two tricyclohexylphosphines in Grubbs' olefin metathesis catalyst with a NHC results in a compound with remarkable reactivity.[1,10a] Second, the complex with the much bulkier IMes ligand (**5**) is more reactive than those with IMe (**2**–**4**) for unhindered alkenes (1-octene and cyclohexene). For tertiary and quaternary alkenes, however, the less hindered IMe complexes (**2**–**4** and **6**) are able to hydrogenate these substrates considerably faster. Therefore, complex **4** is the best catalyst overall of the NHC series (**2**–**5**) since it can hydrogenate all the alkenes tested with rates comparable to **1** at 1 mol% catalyst loading. A very important feature of catalysis using **4** is that the reaction may be carried



Scheme 1 Structures of the complexes synthesized and tested for catalytic homogeneous hydrogenation.

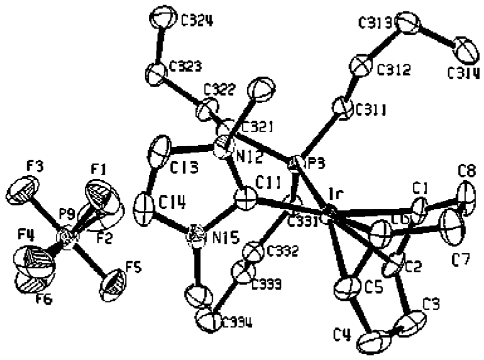


Fig. 1 X-Ray crystal structure of **4**.[11] Selected bond lengths (Å): Ir–P(3) 2.3201(9) , Ir–C(11) 2.050(4), Ir–C(2) 2.180(3), Ir–C(1) 2.195(4), Ir–C(5) 2.216(4), Ir–C(6) 2.217(4).

---

† Electronic supplementary information (ESI) available: experimental section. See http://www.rsc.org/suppdata/cc/b2/b208403a/

DOI: 10.1039/b208403a

out using reagent grade dichloromethane solvent that has not undergone any prior degassing or distillation. The alkene reagents, while stored in the glove box, can be brought out into the air, and simply passed over alumina just before commencement of the reaction to eliminate residual peroxides. Another advantage of this NHC–phosphine series is that the reaction progress can be followed visually. The initial color of the catalytic solution upon addition of hydrogen is red–orange; the color fades somewhat during the course of the reaction, but at ~98% conversion, abruptly becomes almost colorless for ~30 s, and then neon yellow, as shown in the ESI.† The colorless solution is still active, and additional olefin may be added at this step and successfully hydrogenated. The yellow solution, however, is inactive. In the case of **4**, the solvent was removed at the end of the reaction (yellow solution) and the residue dissolved in CD_2Cl_2. The final ^1H NMR revealed at least 12 different carbene resonances and a complex hydride region, with peaks ranging from $\delta -12$ to -33 ppm.

In order to provide insight into the mechanism of the hydrogenation reaction, PHIP ^1H NMR studies were carried out using **4** and [D_8] styrene, following the procedure of Bargon *et al.*[9b] Enhancements in the hydrogenated product are only observed if the two hydrogen atoms from the para-hydrogen molecule are passed in pair-wise fashion to the olefin. The spectrum obtained from the experiment with **4** is shown in Fig. 2 and shows a positive enhancement at δ 2.68, and a corresponding negative enhancement at δ 1.25. The positive and negative pattern indicates that the hydrogenation reaction occurred before placement of the sample in the NMR tube.[9a] This observation suggests that a dihydride mechanism is in operation, but of course, one cannot rule out a parallel monohydride mechanism since it would not appear in the PHIP experiment.[9]

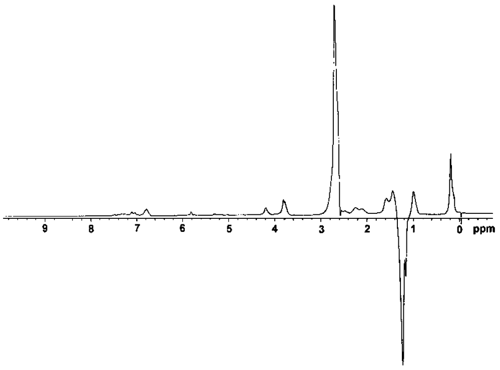


Fig. 2 PHIP ^1H NMR spectra of the hydrogenation of [D_8] styrene with **4**.

In summary, complexes having a combination of phosphine and NHC ligands prove to be very reactive toward the homogeneous catalytic hydrogenation of simple olefins, including hindered substrates. This promising structural motif is presently being expanded upon, and a more detailed analysis of the mechanism of reaction under investigation.

Support from NSF is gratefully acknowledged. J. M. B. is holder of a Camille and Henry Dreyfus New Faculty Award (1997–2002), a Camille and Henry Dreyfus Teacher Scholar Award (2002–2004), a Sloan Foundation Fellowship (2000–2002), and is a Cottrell Teacher–Scholar of Research Corporation (2000–2002). L. D. V. S. thanks the Sloan Foundation for support, and NIH for a training grant. Dr Phil Fanwick is thanked for solving the crystal structure of **4**.

Table 1 Selected results for the catalytic homogeneous hydrogenation of olefins using complexes **1** to **6**

Substrate	Catalyst	Catalyst (mol%)	Time (min)	Conversion[d] (%)
1-Octene	**1**	1[a]	9	100
	1	0.1[b]	41	>99
	2	1[a]	14	100
	3	1[a]	25	100
	4	1[a]	13	100
	4	0.1[b]	62	100
	4	1[a,c]	18	100
	5	1[a]	11	100
	6	1[a]	280	>99
Cyclohexene	**1**	1[a]	9	100
	1	0.1[b]	36	99
	2	1[a]	15	100
	3	1[a]	22	100
	4	1[a]	15	100
	4	0.1[b]	100	>99
	4	1[a,c]	16	100
	5	1[a]	14	100
	6	1[a]	240	>99
1-Methyl-1-cyclohexene	**1**	1[a]	16	99
	1	0.1[b]	60	70
	2	1[a]	30	100
	3	1[a]	60	100
	4	1[a]	21	100
	4	0.1[b]	130	71
	4	1[a,c]	55	94
	5	1[a]	180	100
2,3-Dimethyl-2-butene	**1**	1[a]	40	95
	1	0.1[b]	50	49
	2	1[a]	12	46
	3	1[a]	50	14
	4	1[a]	39	>99
	4	0.1[b]	30	5
	4	1[a,c]	45	13
	5	1[a]	220	19

Conditions:[a] cat, 0.01 mol; olefin, 1.0 mmol; CH_2Cl_2, 5 ml; H_2, 1 atm; temp 25 °C. [b] cat, 0.005 mol; olefin, 5.0 mmol; CH_2Cl_2, 10 ml; H_2, 1 atm; temp 25 °C. [c] Reaction carried out in air. [d] By GC.

Notes and references

1 (*a*) A. Herrmann, *Angew. Chem., Int. Ed.*, 2002, **41**, 1291; (*b*) W. A. Herrmann and C. Köcher, *Angew. Chem., Int. Ed. Engl*, 1997, **36**, 2163; (*c*) J. Huang, H.-J. Schanz, E. D. Stevens and S. P. Nolan, *Organometallics*, 1999, **18**, 2370; (*d*) A. J. Arduengo, H. V. Rasika Dias, R. L. Harlow and M. Kline, *J. Am. Chem. Soc.*, 1992, **114**, 5530.

2 A. J. Arduengo and T. Bannenberg, *Strem Chem.*, 2002, **19**, 2.

3 (*a*) J. Huang, E. D. Stevens, S. P. Nolan and J. L. Petersen, *J. Am. Chem. Soc.*, 1999, **121**, 2674; (*b*) T. Weskamp, V. P. W. Böhm and W. A. Herrmann, *J. Organomet. Chem*, 1999, **585**, 348; (*c*) W. A. Herrmann, J. Schwarz, M. G. Gardiner and M. Spiegler, *J. Organomet. Chem.*, 1999, **575**, 80; W. A. Herrmann, M. Elison, J. Fischer, C. Köcher and G. R. J. Artus, *Chem. Eur. J.*, 1996, **2**, 772.

4 J. Huang, L. Jafarpour, A. C. Hillier, E. D. Stevens and S. P. Nolan, *Organometallics*, 2001, **20**, 2878.

5 T. Weskamp, W. C. Schattenmann, M. Spiegler and W. A. Herrmann, *Angew. Chem., Int. Ed.*, 1998, **37**, 2490; M. Scholl, S. Ding, C. W. Lee and R. H. Grubbs, *Org. Lett.*, 1999, **1**, 953; D. S. Clyne, J. Jin, J. C. Gallucci and T. V. RajanBabu, *Org. Lett.*, 2000, **2**, 1125.

6 S. Bhadur and D. Mukesh, *Homogeneous Catalysis: Mechanisms and Industrial Applications*, John Wiley & Sons, New York, USA, 1994.

7 (*a*) H. M. Lee, T. Jiang, E. D. Stevens and S. P. Nolan, *Organometallics*, 2001, **20**, 1255; (*b*) M. T. Powell, D.-R. Hou, M. C. Perry, X. Cui and K. Burgess, *J. Am. Chem. Soc.*, 2001, **123**, 8878.

8 R. H. Crabtree, H. Felkin and G. E. Morris, *J. Organomet. Chem.*, 1977, **141**, 205; R. H. Crabtree, *Acc. Chem. Res.*, 1979, **12**, 331.

9 (*a*) R. Eisenberg, *Acc. Chem. Res.*, 1991, **24**, 110; (*b*) J. Bargon, J. Kandels and K. Woelk, *Z. Phys. Chem.*, 1993, **180**, 65.

10 T. M. Trnka and R. H. Grubbs, *Acc. Chem. Res.*, 2001, **34**, 18.

11 *Crystal data*: $C_{25}H_{47}F_6IrN_2P_2$, M = 743.81, monoclinic, space group $P2_1/c$ (no. 14), a = 13.9526 (2), b = 9.8549(2), c = 21.4354(4) Å, β = 99.1310(10)°, V = 2910.05(16) $Å^3$, T = 150 K, Z = 4, μ = 4.733 mm^{-1}, 20628 reflections measured, 6834 unique (R_{int} = 0.031) which were used in all calculations. The final $wR(F^2)$ was 0.069 (all data). CCDC 192727. See http://www.rsc.org/suppdata/cc/b2/b208403a/ for crystallographic files in CIF or other electronic format.