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Room temperature tandem hydroamination and hydrosilation/protodesilation catalysis by a tricarbonylchromium-bound iridacycle†

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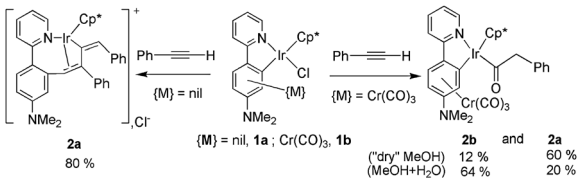
A chromiumtricarbonyl-bound iridacycle displays novel catalytic virtues for the conversion of terminal aromatic alkynes into racemic *N*-phenyl, 1-arylethylamines by tandem hydro-amination and hydrosilation/protodesilation reactions under mild "one pot" conditions.

The principle of atom economy[1] guides nowadays' new developments in the field of catalysis. This principle, which relates to the effective management of reactants and reagents, takes all its substance in the quest for procatalysts capable of performing successive transformations,[2] in a tandem one-pot fashion for example. Our recent investigations of planar chiral[3] iridacycles[4,5] led us to investigate the reactivity of an array of iridacycles in homogenous catalysis. Our attention was particularly attracted by recent reports of Davies *et al.*[6] and Jones *et al.*[7] on the reactivity of iridacycles towards unsaturated organic molecules. Mononuclear iridacycles derived from aryl oxazolines[6] and pyridines[7] may insert alkenes and up to two alkynes to produce new iridacycles. In this communication, we demonstrate that a $Cr(CO)_3$-containing iridacycle[4] promotes readily the hydroamination of terminal alkynes into *N*-phenylimines[8] as well as the hydrosilation/protodesilation[9] of the latter into the corresponding benzylamines, two transformations that can be staged in a one-pot tandem fashion under mild conditions.

A new class of π-complexes of iridacycles[5] was investigated for the possible influence of the electron-withdrawing π-bonded moiety, *i.e.* $Cr(CO)_3$, over possible reactions with terminal alkynes. Preliminary explorations were carried out with iridacycles **1a** and **1b**[5] under the conditions used by Jones *et al.* to promote the dissociation of the Ir–Cl bond, *i.e.* in methanol.[7] Whilst the reaction of complex **1a** with phenylacetylene reproduced the observations of both Jones *et al.*[7] and Davies *et al.*,[6] that is the formation of a product of double insertion, *i.e.* salt **2a** (Scheme 1), the reaction of complex **1b** with the terminal alkyne produced a mixture containing **2a** and a new iridium–acyl complex **2b** (Scheme 1).



Scheme 1 Reaction of mononuclear and binuclear iridacycles **1a** and **1b** with phenylacetylene at room temperature in MeOH for 7 h.

The structure of **2a** was readily established by X-ray diffraction analysis (Fig. 1);† it shows obvious similarities with the structure of the double insertion product reported by Davies *et al.*[6] wherein the insertion sequence for phenylacetylene implies seemingly, the production of a vinyl-type intermediate and the subsequent insertion of the electrophilic α-carbon of the 2-phenylvinylidene ligand.

First principles-based DFT-D3[10] calculations performed on a simplified Cp model of a cationic adduct of **1b** with phenylacetylene upon Ir–Cl bond cleavage indicated that the Gibbs free enthalpy of conversion of a cationic π Ir–alkyne coordinate into an Ir–vinylidene at 298.15 K (gas phase), *i.e.* ΔG_{AB}, amounts around −1.5 kcal mol^{-1} with a moderate activation barrier $\Delta G^{\ddagger}_{AB}$ of *ca.* 17 kcal mol^{-1}, which suggests that

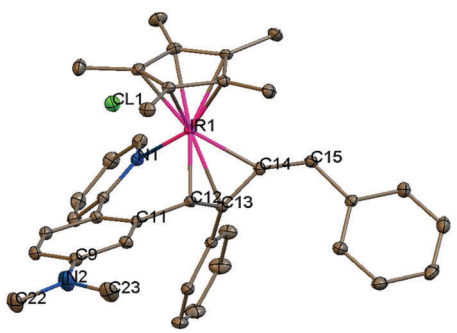


Fig. 1 CSD mercury ellipsoid drawing of the molecular structure of **2a** (30% probability).† Distorted molecule of solvent and atoms of hydrogen have been omitted for the sake of clarity. Selected interatomic distances (Å) and angles (°):Ir1–C14 2.082(2), Ir1–N1 2.103(2), Ir1–C12 2.160(2), Ir1–C13 2.221(2), C11–C12 1.476(3), C12–C13 1.441(3), C13–C14 1.417(3), C14–C15 1.328(3), N1–Ir1–C12 88.91(8).

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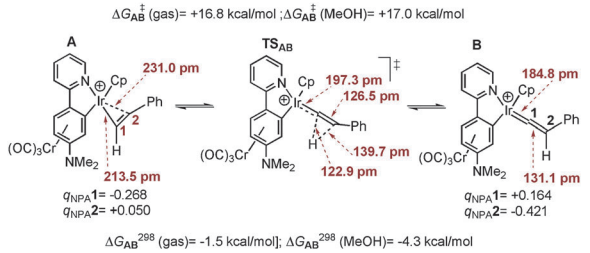
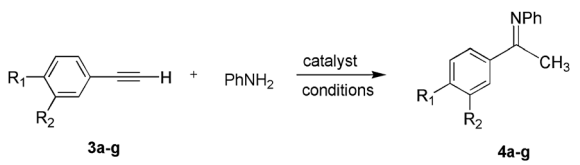
† Electronic supplementary information (ESI) available: Full experimental parts and characterisations; computational details, *i.e.* coordinates, vibrational modes and references. CCDC 893285 (**2a**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2cc35520e



Scheme 2 Equilibration of the alkyne and vinylidene Ir intermediates **A** and **B** in the model ground state and transition state $\mathbf{TS_{AB}}$ (ν(gas) 530.1*i* cm^{-1}, ν(COSMO MeOH) 543.2*i* cm^{-1}) with selected distances for gas phase geometries: Gibbs free enthalpies (298.15 K) of reaction $\Delta G_{\mathbf{AB}}$ and activation Gibbs free enthalpies $\Delta G^{\ddagger}_{\mathbf{AB}}$ were computed in the gas and in the solvated (COSMO MeOH) state at the (ZORA) PBE-D3(0)/all electron TZP level; natural charges at atoms 1 and 2, *i.e.* q_{NPA1} and q_{NPA2}, were obtained from natural population analysis (NPA).

such an interconversion is likely to occur spontaneously in solution, as already suggested by Leong *et al.*[11] In rationalizing the formation of **2a**, this calculation also provides an explanation for the formation of **2b**. Indeed, the "umpolung"[12] occurring at the ethynyl moiety upon vinylidene's formation (Scheme 2) lays the ground for the nucleophilic addition of adventitious water preferably at position 1. Deliberate introduction of large amounts of water in the reaction medium resulted in a drastic reversal of the **2a** : **2b** ratio to *ca.* 1 : 3; no products of catalysed hydration of phenylacetylene were observed though.[13] ^{1}H and ^{13}C NMR and IR spectra of complex **2b** provided sound proofs of the structure of the Ir–acyl **2b** (*cf.* ESI†), the X-ray structure of which is not disclosed in this article for the sake of conciseness. To some extent **2b** presents spectroscopic features similar to Fukuzumi's acyliridium complex (*cf.* ESI†).[13] The peculiar reactivity of **1b** with alkynes in the presence of water led us to consider other potential nucleophiles such as primary amines in order to attempt the formation of Ir–aminovinyl intermediates.

Primary amines such as tBuNH$_2$, PhCH$_2$NH$_2$ and PhNH$_2$ were probed in reactions with phenylacetylene and **1b** in stoichiometric proportions under an inert atmosphere. In the former two cases, no transformation of either the organic substrates or the complex ensued. However in $CDCl_3$, ^{1}H NMR analyses indicated that the alkylamines would form unstable adducts with **1b**, the isolation of which was not sought further.



(1)

In contrast, the reaction of phenylacetylene **3a** with aniline led to the quantitative production of the *Markovnikov* product of hydroamination,[14] *i.e.* *N*-phenylimine **4a**.

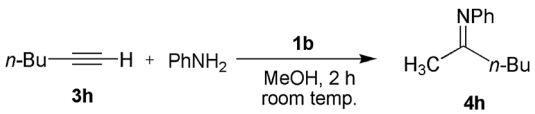
This unexpected result led us to attempt a similar experiment with complex **1a**; the latter happened to convert exclusively into **2a** without any single trace of imine being formed aside (entry 1, Table 1). Complexes **2a** (entry 7, Table 1) and **2b** were found catalytically inactive. This peculiar catalytic property of **1b** was investigated by varying the conditions of the catalysis by first checking the possible promoting action of $NaBArF_4$ in

Table 1 Performance of catalyst **1b** in the hydroamination of **3a** into **4a** (R_1, R_2 = H, eqn (1)) under various experimental conditions

Entry	Catalyst	Solvent	Salt	T (°C)	t (h)	Conversion[d]
1	**1a**[a]	CH_3OH	—	25	10	0
2	**1b**[a]	CH_2Cl_2	$NaBArF_4$[c]	40	12	0
3	**1b**[a]	CH_3Ph	$NaBArF_4$[c]	100	24	30
4	**1b**[b]	CH_3OH	—	65	2	20
5	**1b**[b]	CH_3OH	—	40	1.5	100
6	**1b**[b]	CH_3OH	—	25	2	95
7	**2a**[a]	CH_3OH	—	25	10	0

[a] 5 mol%, 1 eq. aniline. [b] 1 mol%, 1 eq. aniline. [c] 10 mol%. [d] Determined by ^{1}H NMR spectroscopy.

either CH_2Cl_2 or in toluene (Table 1, entries 2 and 3).[15] Only low conversion without decomposition of the catalyst was achieved when toluene and $NaBArF_4$ were used as the solvent and co-catalyst, respectively, at 100 °C. It was found that the best conditions for a quantitative formation of **4a** were by running the reaction in the absence of any ionic co-catalyst, at room temperature in methanol (entries 5 and 6, Table 1). The order of introduction of the reagents was found essential for optimal production of *N*-phenylimines: the best results were achieved when the catalyst was added to a solution of arylacetylene and aniline in freshly distilled methanol. Quantitative transformations could be achieved within 2 h with a molar 1% loading of **1b** at room temperature. Table 2 lists a range of results obtained with various aromatic mono- (**3a–e**) and di-ynes (**3f–g**) as well as with one aliphatic alkyne, *i.e.* 1-hexyne **3h** (eqn (2)). For all aromatic monoalkynes, the yields in imines **4a–e** were quantitative or nearly so. For *para* disubstituted diyne **3f**, the yield in di-imine **5f** was limited to 33% as a probable consequence of the electron-withdrawing deactivating effect of the *para*-imino group at **4f**. In turn, double hydroamination of **3g** into **5g** (entry 7, Table 2) could be achieved in 50% yield, the monohydroamination product **4g** being produced in equal yields.



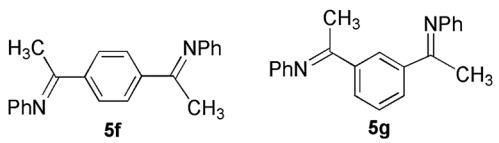


Table 2 Performance of catalyst **1b** in the hydroamination of **3a–h** by aniline at 25 °C in MeOH (eqn (1))

Entry	R_1	R_2	Time (h)	Substrate/ product(s)	Conversion (%)
1	H	H	2[a]	**3a**/**4a**	95
2	H	Me	2[a]	**3b**/**4b**	95
3	OMe	H	2[a]	**3c**/**4c**	100
4	NMe_2	H	2[a]	**3d**/**4d**	100
5	CF_3	H	3[a]	**3e**/**4e**	90
6	C≡CH	H	3[b]	**3f**/**4f**, **5f**	67, 33
7	H	C≡CH	3[b]	**3g**/**4g**, **5g**	50, 50
8	—	—	3[b]	**3h**/**4h**	50

[a] 1 mol% **1b**, 1 eq. aniline. [b] 2.5 mol% **1b**, 2.3 eq. aniline.

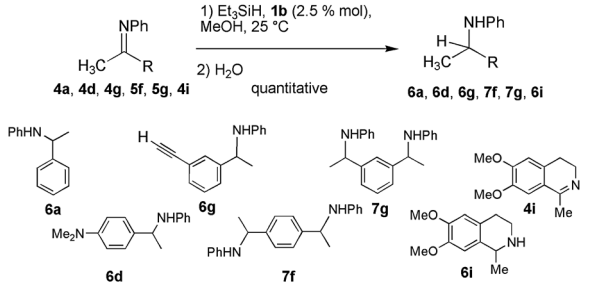
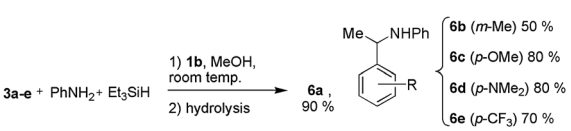


Fig. 2 Quantitative hydrosilation/protodesilation of aromatic imines promoted by **1b**: reactions were carried out with a 1 : 1.2 imine/Et_3SiH ratio.

The influence of substituents *para* to the ethynyl group in arylacetylenes was investigated by competitive experiments, staging the substituted phenylacetylenes **3c–e**, **3a** and a default amount of aniline in a 1 : 1 : 1 ratio in the presence of 1 mol% of **1b** at 25 °C in methanol. Within 3 h each experiment reached quantitative conversion of aniline, leading, respectively, to mixtures containing the product pairs **4c**–**4a**, **4d**–**4a** and **4e**–**4a** in 9 : 1, 4 : 6 and 2 : 8 ratios respectively. This result is consistent with the assumption that the rate determining step could be the addition of aniline to a polarized cationic π Ir–alkyne intermediate akin to **A** (Scheme 2). Further outcome in catalysis for **1b** arose by submitting an array of imines (Fig. 2) to the conditions of hydrosilation/protodesilation, that is to their **1b**-promoted reaction with Et_3SiH in methanol followed by hydrolysis. All attempted reactions led to quantitative conversion of the imines into the corresponding racemic chiral monoamines and diamines, such as **7f**, or the pincer ligand precursor **7g** that was produced as a 1 : 1 mixture of the (*S*,*R*) and (*S**,*S**) diastereomers, and the cyclic alkaloid salsolidine **6i**. The peculiar efficiency of **1b** in promoting hydrosilation was assigned to the possible intervention of an Ir–hydrido intermediate,[4] a key intermediate for the transfer of the hydritic H atom to the electrophilic imine substrate.

Clues for the possible formation of a hydrido–Ir intermediate were obtained in an experiment carried out in dry d_8-THF wherein addition of *N*,*N*-dimethylaminopyridine to a mixture of **1b** with Et_3SiH initiated the release of H_2 and the appearance of a new signal at −15.1 ppm in the ^1H NMR spectrum of the resulting solution, which was assigned to the typical resonance of an Ir-bound hydrido ligand.[4,16] Complex **1b** was also found to readily promote the dehydrogenative methoxylation of Et_3SiH in methanol:[17] the dependence of the rate of release of H_2 gas on the catalyst's concentration was qualitatively evidenced indirectly by following the variation of the voltage raise rate in a modified H_2/air fuel cell[18] (*cf.* ESI†).



Scheme 3 "One pot" transformation of terminal arylethynes into *N*-phenyl,1-arylethylamines promoted by **1b**.

The ability of **1b** to promote sequential catalytic transformations was probed under "one pot" conditions with a series of aromatic terminal alkynes, targeting their conversion to *N*-phenyl,1-arylethylamines. A 1 : 1 : 1.3 mixture of alkyne (**3a–e**), aniline and Et_3SiH was dissolved in methanol in the presence of 2.5 mol% of **1b** at 25 °C. Scheme 3 shows that all conversions in amines **6a–e** are higher than 50% and in three cases they are equal to or higher than 80%.

In conclusion, our study shows that a $Cr(CO)_3$-bound iridacycle such as **1b** can readily promote the tandem transformation of terminal alkynes into *N*-phenylamines. To our knowledge **1b** outperforms other catalysts[15,19] by the mild conditions required particularly for the "one pot" intermolecular hydroamination–hydrosilation/protodesilation of terminal alkynes.[20] These results bear a particular meaning here because the iridacycles in question are planar-chiral by essence. Our ongoing efforts are now focussed on the synthesis of enantio-enriched chiral iridacycles as it appears that iridacycles similar to **1b** display identical catalytic activity (results not shown here) and that other iridacycles are active hydrosilation catalysts.

Notes and references

1 B. M. Trost, *Science*, 1991, **254**, 1471–1477; B. M. Trost, *Acc. Chem. Res.*, 2002, **35**, 695–705; R. A. Sheldon, *Chem. Commun.*, 2008, 3352–3365.
2 S. Fleischer, S. Werkmeister, S. Zhou, K. Junge and M. Beller, *Chem.–Eur. J.*, 2012, **18**, 9005–9010; C. G. Hartung, A. Tillack, H. Trauthwein and M. Beller, *J. Org. Chem.*, 2001, **66**, 6339–6343.
3 J.-P. Djukic, A. Hijazi, H. D. Flack and G. Bernardinelli, *Chem. Soc. Rev.*, 2008, **37**, 406–425.
4 C. Scheeren, F. Maasarani, A. Hijazi, J.-P. Djukic, M. Pfeffer, S. D. Zaric, X.-F. LeGoff and L. Ricard, *Organometallics*, 2007, **26**, 3336–3345; J.-P. Djukic, C. Boulho, D. Sredojevic, C. Scheeren, S. Zaric, L. Ricard and M. Pfeffer, *Chem.–Eur. J.*, 2009, **15**, 10830–10842.
5 J.-P. Djukic, W. Iali, M. Pfeffer and X.-F. LeGoff, *Chem. Commun.*, 2011, **47**, 3631–3633; J.-P. Djukic, W. Iali, M. Pfeffer and X.-F. LeGoff, *Chem.–Eur. J.*, 2012, **18**, 6063–6078.
6 D. L. Davies, O. Al-Duaij, J. Fawcett and K. Singh, *Organometallics*, 2010, **29**, 1413–1420.
7 L. Li, Y. Jiao, W. W. Brennessel and W. D. Jones, *Organometallics*, 2010, **29**, 4593–4605.
8 F. Pohlki and S. Doye, *Chem. Soc. Rev.*, 2003, **32**, 104–114; R. Severin and S. Doye, *Chem. Soc. Rev.*, 2007, **36**, 1407–1420.
9 L. D. Field, B. A. Messerle and S. L. Rumble, *Eur. J. Org. Chem.*, 2005, 2881–2883.
10 S. Grimme, J. Antony, S. Ehrlich and H. Krieg, *J. Chem. Phys.*, 2010, **132**, 154104.
11 E. Kumaran and W. K. Leong, *Organometallics*, 2012, **31**, 4849–4853.
12 D. Seebach, *Angew. Chem., Int. Ed. Engl.*, 1979, **18**, 239–258.
13 S. Ogo, K. Uehara, T. Abura, Y. Watanabe and S. Fukuzumi, *J. Am. Chem. Soc.*, 2004, **126**, 16520–16527.
14 M. Nobis and B. Driessen-Holscher, *Angew. Chem., Int. Ed.*, 2001, **40**, 3983–3985.
15 R.-Y. Lai, K. Surekha, A. Hayashi, F. Ozawa, Y.-H. Liu, S.-M. Peng and S.-T. Liu, *Organometallics*, 2007, **26**, 1062–1068.
16 Y. Hu, L. Li, A. P. Shaw, J. R. Norton, W. Sattler and Y. Rong, *Organometallics*, 2012, **31**, 5058–5064.
17 L. D. Field, B. A. Messerle, M. Rehr, L. P. Soler and T. W. Hambley, *Organometallics*, 2003, **22**, 2387–2395.
18 C. Boulho and J.-P. Djukic, *Dalton Trans.*, 2010, **39**, 8893–8905.
19 E. Kumaran and W. K. Leong, *Organometallics*, 2012, **31**, 1068–1072.
20 L. D. Field, B. A. Messerle and S. L. Wren, *Organometallics*, 2003, **22**, 4393–4395.