Available online at www.sciencedirect.com

Journal of Catalysis 238 (2006) 497–501

JOURNAL OF CATALYSIS

www.elsevier.com/locate/jcat

Priority Communication

Gold (I) and (III) catalyze Suzuki cross-coupling and homocoupling, respectively

C. González-Arellano [a,c], A. Corma [b,*], M. Iglesias [c], F. Sánchez [a]

[a] *Instituto de Química Orgánica General, CSIC, C/Juan de la Cierva 3, 28006 Madrid, Spain*
[b] *Instituto de Tecnología Química, UPV-CSIC, Universidad Politécnica de Valencia, Avda. de los Naranjos s/n, 46022 Valencia, Spain*
[c] *Instituto de Ciencia de Materiales de Madrid, CSIC, C/Sor Juana Inés de la Cruz s/n, Cantoblanco, 28049 Madrid, Spain*

Received 25 October 2005; revised 7 December 2005; accepted 12 December 2005

Abstract

Trinuclear triphenylphosphine **1,2Au(I)** complexes with the [N,N,O]-tridentate unsymmetrical Schiff bases (**1**,**2**) catalyze the Suzuki cross-coupling reaction to afford nonsymmetrical biaryls in good yields, whereas the **1,2Au(III)** complexes give only arylboronic homocoupling.

Keywords: Gold catalysts for carbon–carbon bond formation; Gold(I) catalysts for Suzuki cross-coupling; Gold(III) catalysts for homocoupling C–C formation

1. Introduction

Gold was believed to be chemically inert, and with very few exceptions [1] the possibilities of homogeneous and heterogeneous gold catalysts for organic reactions were not considered. Recent reports have shown that gold salts, specifically Au(III), can act as a Lewis acid catalyst for a large variety of reactions [2]. Solid gold catalysts, on the other hand, can be recycled, and when prepared in the form of smaller clusters (particle size $\leqslant 5$ nm) are highly active and selective for reactions such as CO oxidation in the presence of H_2 [3,4], water–gas shift [5], alcohol oxidations [6], and some C–C forming reactions [7]. Gold in homogeneous complexes [8] has shown possibilities for several catalytic reactions, including asymmetric aldol condensation, and the asymmetric hydrogenation of alkenes and imines [9]. More specifically, it has been recently shown [10] that Au(III) complexes were active and selective catalysts for carrying out the homocoupling of different aryl boronic acids. However, Au(III), unlike Pd complexes, were not able to catalyze cross-coupling reactions.

Transition metal-catalyzed cross-coupling reactions are useful tools in organic synthesis for constructing C–C bonds. Among these, the coupling of an aryl halide with an organoboron reagent—the Suzuki reaction—has emerged as an interesting reaction because of the mild reaction conditions required [11]. Pd–phosphine complexes [12] have been the most commonly used catalysts for the Suzuki reaction. However, alternative ligands such as N-heterocyclic carbenes [13], imidazol-2-ylidenes [14], and diazabutadienes [15] have been used in Suzuki coupling reactions. Very recently, we have shown that phenolic Shiff-base complexes of Au(III) catalyze the homocoupling of aryl boronic acids, but were unable to catalyze the Suzuki cross-coupling [10]. Because Pd(0) is quite an effective catalysts for the above reaction, and Au(I) has the same d^{10} electronic configuration that Pd(0), we considered that Au(I) complexes may be active catalysts for performing the Suzuki cross-coupling.

In the present work, new types of Au(I) complexes were prepared and characterized. They were found to be active and selective for catalyzing Suzuki cross-coupling, whereas Au(III) complexes with same ligands can only catalyze the arylboronic homocoupling.

2. Experimental

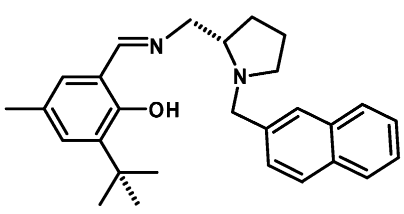
2.1. Catalyst preparation

2-*tert*-Butyl-4-methyl-6-[({[(2*S*)-1-(2-naphthylmethyl)pyrrolidinyl])methyl}-imino)methyl]-phenol (**1**) was used as lig-

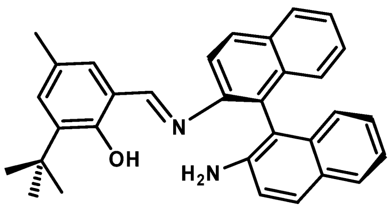
---

[*] Corresponding author. Fax: +34 96 3877809.
E-mail address: acorma@itq.upv.es (A. Corma).

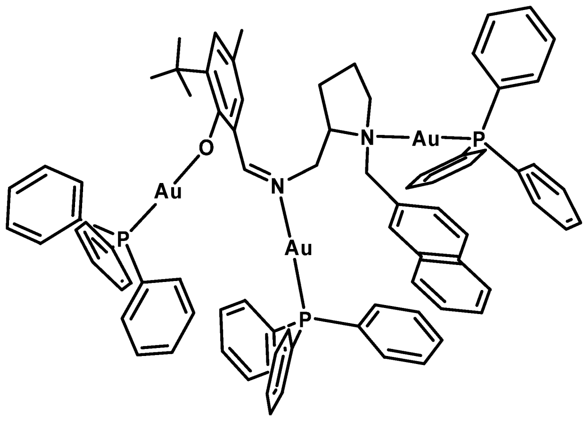
0021-9517/$ – see front matter © 2005 Elsevier Inc. All rights reserved.
doi:10.1016/j.jcat.2005.12.015



1



2



1Au(I)

Fig. 1. Ligands and proposed structure for **Au(I)**-complexes.

and with Au(I) and Au(III) (Fig. 1). In this type of potentially tridentate ligands, there are two types of nitrogen donor atoms and one oxygen phenolate [16]. The nitrogen on the pyrrolidine ring is expected to act as a hemilabile ligand, while the Schiffs base nitrogen and oxygen act as the principal donors. Along with ligand **1**, a binaphthyl derivative (**2**) was also examined for comparison.

The preparation of metal complexes was carried out under dinitrogen by conventional Schlenk tube techniques. Solvents were carefully degassed before use, and the $AuCl(PPh_3)$ was prepared as described previously [17]. Au(I) complexes were synthesized following Eqs. (1) and (2):

$$(C_{28}H_{34}N_2)O^-K^+ + AuCl(PPh_3) \rightarrow \big[(C_{28}H_{34}N_2)O(Au(PPh_3)_3)\big][Cl]_2 + KCl, \quad (1)$$

$$(C_{32}H_{30}N_2)O^-K^+ + AuCl(PPh_3) \rightarrow \big[(C_{32}H_{28}N_2)O(Au(PPh_3)_3)\big]Cl + KCl. \quad (2)$$

Then $AuCl(PPh_3)$ (1 mmol) in THF was added to a solution of the phenolate ligand (1 mmol) in THF (20 ml) at 40 °C. The resultant mixture was stirred for 2 h, cooled to room temperature, filtered, and then concentrated under vacuum. The residue was extracted with dichloromethane and precipitated with pentane, washed several times, filtered, and dried to afford the respective yellow brown, air-stable solids complexes in high yields. Properties, analytical and characteristics of the complexes are as follows.

2.1.1. *$[(C_{28}H_{34}N_2)O(Au(PPh_3)_3)]Cl_2$ [**1Au(I)**]*

Color: orange brown. Yield: >85%. m.p: 100 °C (dec.). $\Lambda_M > 200\ \Omega^{-1}\,cm^2\,mol^{-1}$. $C_{82}H_{78}Au_3Cl_2N_2OP_3$ calcd. for (1862.2): C, 52.9; H, 4.2; N, 1.5; P, 5.0; Au, 31.7; found: C, 52.8; H, 4.7; N, 2.0; P, 5.2; Au, 32.1%. IR (KBr, cm^{-1}): $\nu = 1629$, 1602 (C=N, C=C). UV–vis (λ, nm): 424, 375, 337, 296, 267, 231. ^1H RMN (CD_3OD, ppm): $\delta = 8.24$ (H, s, CH=N); 7.80–6.96 (m, H_{arom}); 4.04–3.45 (4H, m, CH_{2Bz}, $H_{5,5'}$); 3.53–3.49 (1H, m, H_2); 3.00–2.46 (2H, m, $CH{=}NCH_2$); 2.25–1.88 (7H, m, CH_3, $H_{4,4'}$, $H_{3,3'}$); 1.39 (9H, s, $C(CH_3)_3$). ^{13}C RMN (CD_3OD, ppm): $\delta = 169.17$ (C–O–Au); 158.63 (CH=N); 135.66, 133.54, 131.16, 130.41, 130.24, 128.97 (C_{arom}); 67.30 (C_2); 30.89 ($C(CH_3)_3$); 30.32 ($C(CH_3)_3$); 24.16 (CH_3); 21.05 (C_4). ^{31}P NMR (CD_3Cl, ppm): $\delta = 33.79$. EM (m/z): 1377 $[(AuPPh_3)_3]^+$, 415 (L+1).

2.1.2. *$[(C_{32}H_{28}N_2)O(Au(PPh_3)_3]Cl$ [**2Au(I)**]*

Color: orange. Yield: >90%. m.p: 170 °C (dec.). $\Lambda_M = 119\ \Omega^{-1}\,cm^2\,mol^{-1}$. $C_{86}H_{73}Au_3ClN_2OP_3$ calcd. for (1869.79): C, 55.2; H, 3.9; N, 1.5; P, 5.0; Au, 31.6; found: C, 54.8; H, 3.6; N, 1.1; P, 4.6; Au, 31.9%. IR (KBr, cm^{-1}): $\nu = 1615$ (C=N, C=C). UV–vis (λ, nm): 453, 413, 375, 321, 294, 266, 235. ^1H RMN (CD_3Cl, ppm): $\delta = 7.93$–7.38 (14H + 45H, m, H_{arom}, CH=N); 1.40 (3H, s, CH_3); 1.29 (9H, s, $C(CH_3)_3$). ^{13}C RMN (CD_3Cl, ppm): $\delta = 168.1$ (C–O–Au); 152.63 (CH=N); 135.35, 134.48, 130.56 (C_{arom}); 33.90 ($C(CH_3)_3$); 33.46 ($C(CH_3)_3$); 20.50 (CH_3). ^{31}P NMR (CD_3Cl, ppm): $\delta = 33.79$. EM (m/z): 1833 (M^+–Cl), 1377 $[(AuPPh_3)_3{}^+]$, 459 $[AuPPh_3]^+$.

IR spectra were recorded with a Bruker IFS 66v/S spectrophotometer (range, 4000–200 cm^{-1}) in KBr pellets. ^{1}H NMR, ^{13}C NMR, ^{31}P NMR spectra were taken with Varian XR300 and Bruker 200 spectrometers. Chemical shifts being referred to tetramethylsilane (internal standard) or to PO_4H_3 (^{31}P).

2.2. Catalytic experiments

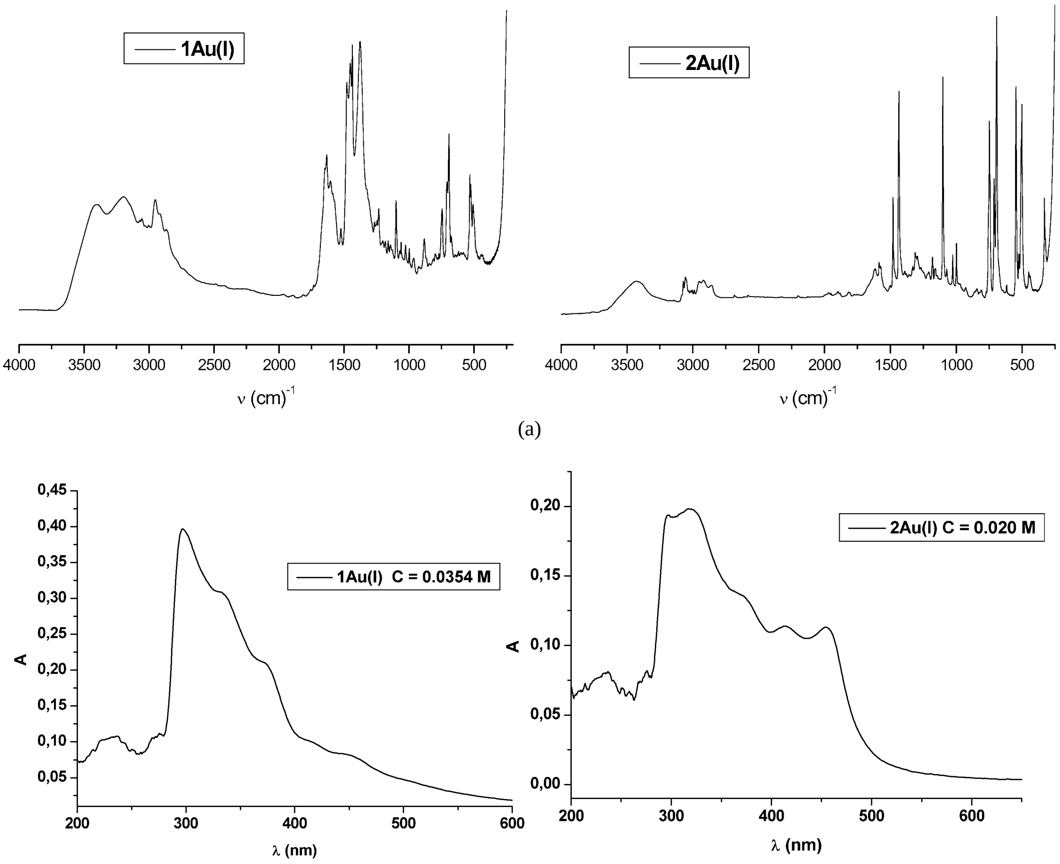
The reaction was carried out in a 25-ml vessel at 130 °C for 20–180 min. In a typical run, a mixture of aryl halide (10 mmol), boronic acid (15 mmol), aqueous potassium carbonate or phosphate (20 mmol), and catalyst (0.3 mmol) in 3 ml of *o*-xylene was stirred for the desired time. The solution was allowed to cool, and a 1:1 mixture of ether/water (20 ml) was added. The organic layer was washed, separated, further washed with another 10 ml portion of diethyl ether, dried with anhydrous $MgSO_4$, and filtered. The solvent and volatiles were completely removed under vacuum to give the crude product, which, when subjected to column chromatographic separation, resulted in pure compounds. The reaction was followed by gas chromatography–mass spectroscopy (GC–MS). GC analyses were performed in a Hewlett-Packard 5890 II with a flame ionization detector and/or a Hewlett-Packard G1800A with a quadrupole mass detector using a cross-linked methylsilicone column.

3. Results and discussion

The complexes were identified by elemental analysis, MS, and nuclear magnetic resonance (NMR) spectroscopy. The mass spectrum (by electro-spray mass spectrometry) shows the ion molecular, $[AuPPh_3{}^{+}]$, $[(AuPPh_3)_3{}^{+}]$, and peaks from the fragments due to elimination of the phosphine ligand. The high stability of these complexes originates from the donor capacity of the imine nitrogen atom assisting in the bonding of the second gold atom [18].

Fourier transform infrared spectra (Fig. 2a) are characteristic of the binding of imine nitrogen. The 1600 cm^{-1} frequencies can be assigned to C=C and azomethine C=N vibrations, shifted to lower wavenumbers (relative to the free ligands) due to N-coordination of the imine [19]. The absence of the ν(OH) band (present in the spectra of the free ligands at ~3430 cm^{-1}) is in accordance with loss of the –OH proton. The infrared spectra also show bands assigned to the phosphine ligand. New bands in the 500–600 cm^{-1} region are ascribed to ν(M–O).

The electronic absorption spectra for all complexes (Fig. 2b) were obtained using 10^{-3}–10^{-5} M dichloromethane solutions in the 200–800 nm range. The complexes show several band maxima in the UV region agreeing with the assignment of the bands as intraligand $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$, transitions in the aromatic ring, azomethine group, and charge-transfer transition [20]. The higher molar extinction coefficient of the bands in



(a)

(b)

Fig. 2. (a) FTIR and (b) electronic absorption spectra for Au(I) complexes.

Table 1
Influence of ligands on Au(I) reactivity for Suzuki reactions: Ph–I + Ar–$B(OH)_2 \rightarrow$ Ph–Ar + Ar–Ar

	1Au(I)		**2Au(I)**	
Ar	Conversion (%)	Selectivity[a] (%)	Conversion (%)	Selectivity[a] (%)
Ph	80 (2)	–	84 (2)	–
3-BrPh	41 (3)	50	48 (2)	86
4-BrPh	30 (3)	70	53 (3)	88
4-MeOPh	44 (3)	92	49 (3)[b]	86
3-HCOPh	40 (2)	85	61 (1.5)	100
4-HCOPh	25 (1.5)	100	42 (1.5)	100

Ratio catalyst: IPh = 1:30, IPh (1 mmol), aryl boronic (1.5 mmol), K_3PO_4 (2 mmol).

[a] Cross-coupling/conversion.

[b] Reaction with BrPh yields only homocoupling product. Reaction with K_2CO_3 as base gives 18% cross-copling with selectivity 100%. In parenthesis, reaction time in hours.

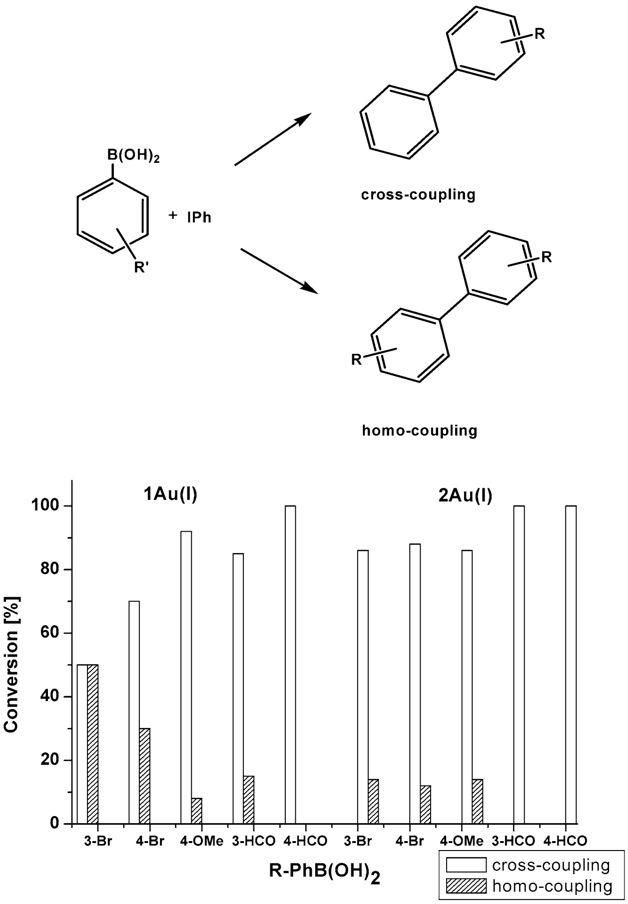


Fig. 3. Suzuki reaction results for Au(I) complexes.

the 260–350 nm range may be due to the coincidence of charge transfer, $d \rightarrow \pi^*$, and intraligand $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$ transitions. The bands in the 400–500 nm region correspond to d–d transitions and MLCT bands.

The diamagnetic gold complexes presented here were characterized by ^1H, ^{13}C, and ^{31}P NMR spectroscopy (data given in the Catalyst preparation section). All assignments are based on several correlations in the two-dimensional spectra. In all cases, the spectra show the simultaneous occurrence of two set of signals, which are assigned on the one hand to the substituted benzaldimine entity and on the other hand to the aliphatic (**1**) or aromatic (for **2**) part of the ligand. In the ^1H NMR spectra, all of the resonances are high field shifted compared with the uncoordinated ligand and are in agreement with metallation of the ligand with coordination of the metal atom via the imine nitrogen atom. The most noticeable shifts involve $HC{=}N$, $C{=}N{-}CH_2N{-}$, $H_{2'}$, and $H_{5'}$. Deprotonation of the –OH group was confirmed by the absence of OH resonances in the ^1H spectra. The resonance corresponding to the $HC{=}N$ proton appears as a singlet ($\delta = 8.5$–7.2 ppm) shifted to high field due to the coordination of the imine group to the metal atom through the lone pair of the nitrogen atom [21]. The ^1H NMR spectrum shows the signals of the PPh_3 protons as a multiplet at $\delta = 7$–8 ppm. The ^{13}C NMR spectra show the signals assigned to the $C{=}N$ carbon high field shifted and C_1 at $\delta \approx 162$ downfield shifted, confirming that metallation occurred. ^{31}P NMR spectra show a signal at $\delta \approx 34$ ppm. Structures of complexes **1Au(I)** and **2Au(I)** that agree with the spectroscopic characterization are presented in Fig. 1. Linear structures in which the gold is trinuclear can be observed.

The Au(I) complexes were studied for the Suzuki cross-coupling of Br–Ph and I–Ph with a series of aryl boronic acids. The standard reaction conditions were applied to a series of catalysts; the conversions are tabulated in Table 1. In our experiments, we chose K_3PO_4 as mild base, because with K_2CO_3, longer reaction times are needed to obtain reasonable conversions.

The general utility of the reaction conditions with a variety of aryl boronic acid substrates (aryl=Ph, 3- and 4-BrPh, 4-MeOPh, 4-MePh, 3- and 4-HCOPh) and aryl halides (BrPh, IPh) was studied. Au(I) complexes with phenyl bromide are ineffective, yielding the homocoupling compound as a principal product. On the other hand, gold (I) complex with ligand **1**, which is less electron-rich than **2**, gives lower activity toward the Suzuki reaction (Table 1). The effects of electron-donating and electron-withdrawing substituents in the boronic acid on reactivity are also given in Table 1. In general, moderate to excellent yields and good selectivity toward the cross-coupling product are found with Au(I) complexes (Fig. 3). The best reactivity is found with 3- or 4-formylphenylboronic acid as the substrate. It is noteworthy that when **1,2Au(III)** complexes are used as catalysts for several of the reactions, only homocoupling of boronic acids is observed (Fig. 3) [9].

For comparison purposes, **2Pd(II)** and $Pd(PPh_3)_4$ complexes were prepared and tested under the same reaction conditions (Table 2). Results (Tables 1 and 2) show that activity and selectivity of **2Au(I)** and Pd complexes are similar, although the $Pd(PPh_3)_4$ is systematically more active. Nevertheless, it is interesting to see that Au(I), which has the same d^{10} electronic structure as Pd^0, is able to catalyze the cross-coupling reaction with high selectivity. On the other hand, changing the charge of the gold atom [Au(III)] makes it possible to selectively catalyze the homocoupling reaction.

Table 2
Suzuki reactions with the Pd complexes as catalysts Ph–I + Ar–$B(OH)_2$ → Ph–Ar + Ar–Ar

	Pd complexes			
	$Pd(PPh_3)_4$		Pd(II)	
Ar	Conversion (%)	Selectivity[a] (%)	Conversion (%)	Selectivity[a] (%)
Ph	100 (1)	100	90 (1.5)	89
3-BrPh	66 (3)	88	–	–
4-BrPh	71 (1.5)	96	–	–
4-MeOPh	66 (1.5)	75	48 (0.5)	12
3-HCOPh	78 (1.5)	100	68 (3)	100
4-HCOPh	69 (1.5)	100	39 (3)	100

[a] Ratio catalyst:IPh = 1:30, IPh (1 mmol), aryl boronic (1.5 mmol), K_3PO_4 (2 mmol). In parenthesis, reaction time in hours

4. Conclusion

Two new Au(I)-Schiff base complexes have been synthesized and characterized. These are efficient catalysts for Suzuki coupling reactions of iodobenzene and several aryl boronic acids to give nonsymmetrical biaryls. Their activity and selectivity is similar to the corresponding Pd complexes, indicating that Au(I) with the same d^{10} configuration as Pd(0) can catalyze reactions typically catalyzed by palladium. On the other hand, the same Shiff base complexes of Au(III) catalyze arylboronic homocoupling with 100% selectivity.

Acknowledgments

The authors thank Ministerio de Educación y Ciencia (project MAT2003-07945-C02-01 and 02) and the Auricat EU Network (HPRN-CT-2002-00174) for financial support.

References

[1] (a) G.J. Hutchings, Catal. Today 100 (2005) 55;
(b) G.J. Hutchings, Gold Bull. 37 (2004) 3.
[2] (a) A. Corma, H. García, Chem. Rev. 103 (2003) 4037;
(b) Ch. Wei, Ch.-J. Li, J. Am. Chem. Soc. 125 (2003) 9584;
(c) X. Yao, Ch.-J. Li, J. Am. Chem. Soc. 126 (2004) 6884;
(d) G. Dyker, Angew. Chem. Int. Ed. 39 (2000) 4237, and references therein.
[3] (a) M. Haruta, T. Kobayashi, H. Sano, N. Yamada, Chem. Lett. (1987) 405;
(b) M. Haruta, N. Yamada, T. Kobayashi, S. Iijima, J. Catal. 115 (1989) 301.
[4] (a) B.C. Gates, J. Guzman, Angew. Chem. Int. Ed. 42 (2003) 690;
(b) S. Carrettin, P. Concepción, A. Corma, J.M. López-Nieto, V.F. Puntes, Angew. Chem. Int. Ed. 43 (2004) 2538;
(c) J. Guzman, B.C. Gates, J. Am. Chem. Soc. 126 (2004) 2672;
(d) A. Luengnaruemitchai, D.T.K. Thoa, S. Osuwan, E. Gulari, Int. J. Hydrogen Energy 30 (2005) 981.
[5] J. Hua, Q. Zheng, Y. Zheng, K. Wei, X. Lin, Catal. Lett. 102 (2005) 99.
[6] (a) A. Corma, A. Abad, P. Concepción, H. García, Angew. Chem. Int. Ed. 44 (2005) 4066;
(b) F. Porta, L. Prati, M. Rossi, G. Scari, J. Catal. 211 (2002) 464.
[7] (a) S. Carrettin, J. Guzmán, A. Corma, Angew. Chem. Int. Ed. 44 (2005) 2242;
(b) A.S.K. Hashmi, L. Schwarz, J.-H. Choi, T.M. Frost, Angew. Chem. Int. Ed. 39 (2000) 2285.
[8] (a) A.S.K. Hashmi, J.P. Weyrauch, M. Rudolph, E. Kurpejovic, Angew. Chem. Int. Ed. 43 (2004) 6545;
(b) A.S.K. Hashmi, Gold Bull. 37 (2004) 51, and references therein.
[9] (a) Y. Ito, M. Sawamura, T. Hayashi, J. Am. Chem. Soc. 108 (1986) 6405;
(b) C. González-Arellano, A. Corma, M. Iglesias, F. Sánchez, Chem. Commun. (2005) 3451.
[10] C. González-Arellano, A. Corma, M. Iglesias, F. Sánchez, Chem. Commun. (2005) 1990.
[11] (a) J. Hassan, M. Sévignon, Ch. Gozzi, E. Schulz, M. Lemaire, Chem. Rev. 102 (2002) 1359;
(b) A. Suzuki, J. Organomet. Chem. 576 (1999) 147;
(c) N. Miyaura, A. Suzuki, Chem. Rev. 95 (1995) 2457;
(d) A. Suzuki, in: F. Diederich, P.T. Stang (Eds.), Metal-Catalysed Cross-Coupling Reactions, Wiley–VCH, Weinheim, 1998, pp. 49–97.
[12] (a) D.W. Old, J.P. Wolfe, S.L. Buchwald, J. Am. Chem. Soc. 120 (1998) 9722;
(b) J.P. Wolfe, S.L. Buchwald, Angew. Chem. Int. Ed. 38 (1999) 2413;
(c) J.P. Wolfe, R.A. Singer, B.H. Yang, S.L. Buchwald, J. Am. Chem. Soc. 121 (1999) 9550;
(d) J. Yin, S.L. Buchwald, J. Am. Chem. Soc. 122 (2000) 12051;
(e) J. Yin, M.P. Rainka, X.-X. Zhang, S.L. Buchwald, J. Am. Chem. Soc. 124 (2002) 1162;
(f) T.E. Barder, S.D. Walker, J.R. Martinelly, S.L. Buchwald, J. Am. Chem. Soc. 127 (2005) 4685.
[13] (a) V.P.W. Bohm, C.W.K. Gstottmayr, T. Weskamp, W.A. Herrmann, J. Organomet. Chem. 595 (2000) 186;
(b) O. Navarro, R.A. Kelly III, S.P. Nolan, J. Am. Chem. Soc. 125 (2003) 16194.
[14] C. Zhang, J. Huang, M.L. Trudell, S.P. Nolan, J. Org. Chem. 64 (1999) 3804.
[15] G.A. Grasa, A.C. Hilier, S.P. Nolan, Org. Lett. 3 (2001) 1077.
[16] C. González-Arellano, E. Gutiérrez-Puebla, M. Iglesias, F. Sánchez, Eur. J. Inorg. Chem. (2004) 1955.
[17] M.I. Bruce, B.K. Nicholson, O.B. Shawkataly, Inorg. Synth. 26 (1989) 325.
[18] A. Kolb, P. Bissinger, H. Schmidbaur, Inorg. Chem. 32 (1993) 5132.
[19] (a) H. Onoue, I. Moritani, J. Organomet. Chem. 43 (1972) 431;
(b) H. Onoue, K. Minami, K. Nakagawa, Bull. Chem. Soc. Jpn. 43 (1970) 3480.
[20] T.N. Sorrell, W.E. Allen, P.S. White, Inorg. Chem. 34 (1995) 952.
[21] Y. Ustynyuk, V.A. Chertov, J.V. Barinov, J. Organomet. Chem. 29 (1971) C53.