Available online at www.sciencedirect.com

SCIENCE DIRECT®

Journal of Organometallic Chemistry 664 (2002) 77–84

Journal of Organometallic Chemistry

www.elsevier.com/locate/jorganchem

New complexes of palladium(II) with chelating heterocyclic nitrogen ligands. Characterization and catalytic activity in CO–styrene copolymerization. Crystal structure of $[Pd(bipy)_2][BAr'_4]_2$, $Ar' = [3,5\text{-}(CF_3)_2C_6H_3]$

Sergio Stoccoro [a,*], Giuseppe Alesso [a], Maria Agostina Cinellu [a], Giovanni Minghetti [a], Antonio Zucca [a], Amaia Bastero [b], Carmen Claver [b,*], Mario Manassero [c,*]

[a] *Dipartimento di Chimica di Sassari, Via Vienna 2, 07100 Sassari, Italy*
[b] *Departament de Quimica Fisica i Inorganica, Universitat Rovira i Virgili, Pl. Imperial Tarraco 1, 43005 Tarragona, Spain*
[c] *Dipartimento di Chimica Strutturale e Stereochimica Inorganica, Università di Milano, Centro C.N.R., 20133 Milan, Italy*

Received 30 July 2002; received in revised form 20 September 2002; accepted 20 September 2002

Abstract

New bis-chelated palladium(II) derivatives $[Pd(bipy^R)_2]^{2+}$ and $[Pd(bipy)(bipy^R)]^{2+}$ (bipy = 2,2′-bypiridine, $bipy^R$ = 6-Me, 6-Et, 6-*i*-Pr-2,2′-bipyridine) have been isolated as $[BAr'_4]^-$ salts ($Ar' = [3,5\text{-}(CF_3)_2C_6H_3]$) and tested as catalyst precursors in the CO–styrene or 4-*tert*-butylstyrene (TBS) copolymerization. The comparison of their activity with that of $[Pd(bipy)_2][BAr'_4]_2$ prepared for comparative purpose shows that the presence of a 6-substituent on the bipy has a negative effect. On the other hand, comparison of the activities of $[Pd(bipy)_2][BAr'_4]_2$ and $[Pd(bipy)_2][PF_6]_2$, reported to be one of the best catalytic precursors for this reaction, shows that the $[BAr'_4]^-$ anion increases the activity under various reaction conditions. The results obtained with $[Pd(bipy)_2][BAr'_4]_2$ at low pressure (p_{CO} = 10 atm) are among the best reported for this type of precatalysts. A study related to the use of 2,2,2-trifluoroethanol (TFE), as solvent, allows the optimisation of the amount of alcohol required for the copolymerization reaction. The X-ray structure of $[Pd(bipy)_2][BAr'_4]_2$ shows that the conformation of the cation is similar to that observed in the corresponding $[BF_4]^-$ salt, but remarkably different from that of $[Pd(bipy)_2][PF_6]_2$.

Keywords: Catalysis; Copolymerization; Styrene; Palladium complexes; Nitrogen ligands; X-ray

1. Introduction

It is known that palladium(II) complexes containing bidentate nitrogen ligands and weakly or not coordinating anions are efficient catalyst precursors in the alternating copolymerization of styrene and carbon monoxide [1]. During the last years this catalytic process has been extensively investigated under various conditions. The effect of a number of parameters, e.g. catalyst precursor, p_{CO}, temperature, solvent, nature of the chelating ligand, etc. has been considered and mechanistic studies have been carried out [2].

Two different types of isolated cationic Pd(II) precursors have been shown to be efficient in this catalytic reaction. Cationic complexes of formula $[Pd(CH_3)(L–L)(S)]X$ (S = solvent), which are active in aprotic solvent [2c], and species containing one or two chelating ligands, $[Pd(L–L)(S)_2]X_2$ or $[Pd(L–L)_2]X_2$, respectively, which need alcoholic media to start copolymerization [2d,2e,2k,2l,2m]. Today cationic bis-chelated complexes with unsubstituted 2,2′-bipyridine or 1,10-phenanthroline ligands and $[PF_6]^-$ as counter anion are reported to be the most effective catalytic precursors [2k,2m]. The

---

* Corresponding authors

E-mail addresses: stoccoro@ssmain.uniss.it (S. Stoccoro), claver@quimica.urv.es (C. Claver), m.manassero@csmtbo.mi.cnr.it (M. Manassero).

PII: S0022-328X(02)01966-6

effect of the substituents on the nitrogen ligands has attracted scant attention [2d,2e,2p,3]. Here we report on the synthesis of several bis-chelated Pd(II) derivatives with 6-R-substituted-2,2′-bipyridines (R = Me, bipy^{Me}; R = Et, bipy^{Et}; R = *i*-Pr, $\text{bipy}^{i\text{-Pr}}$) as $[\text{BAr}'_4]^-$ salts ($\text{Ar}' = [3,5\text{-}(\text{CF}_3)_2\text{C}_6\text{H}_3]$). Two series of complexes have been synthesized, namely $[\text{Pd}(\text{bipy}^{\text{R}})_2][\text{BAr}'_4]_2$ (bipy^{Me}, **1**, bipy^{Et}, **2**, $\text{bipy}^{i\text{-Pr}}$, **3**) and $[\text{Pd}(\text{bipy})(\text{bipy}^{\text{R}})][\text{BAr}'_4]_2$ (**4**, **5**, **6**) (R = Me, Et, *i*-Pr, respectively) and tested as catalyst precursors in the CO–styrene and/or 4-*tert*-butylstyrene (TBS) copolymerization. Their activity is compared with those of $[\text{Pd}(\text{bipy})_2][\text{BAr}'_4]_2$ (**7**) and $[\text{Pd}(\text{bipy})_2][\text{PF}_6]_2$ (**8**). The amount of 2,2,2-trifluoroethanol (TFE), as efficient solvent in this reaction, has been optimized for this catalytic system.

In addition, the X-ray structure of $[\text{Pd}(\text{bipy})_2][\text{BAr}'_4]_2$ has been solved resulting similar to that of the corresponding $[\text{BF}_4]^-$ salt [2k], but remarkably different from that of $[\text{Pd}(\text{bipy})_2][\text{PF}_6]_2$ [4].

2. Results and discussion

The ligands bipy^{R} (R = Me, Et, *i*-Pr) have been obtained according to published methods [5,6]. The new $[\text{BAr}'_4]^-$ salts of the bis-chelated palladium complexes have been synthesized through the two steps reaction (reaction 1):

$$\text{Na}_2[\text{PdCl}_4] + \text{bipy}^{\text{R}} \rightarrow [\text{Pd}(\text{bipy}^{\text{R}})\text{Cl}_2] + 2\text{NaCl}$$

$$[\text{Pd}(\text{bipy}^{\text{R}})\text{Cl}_2] + \text{bipy}^{\text{R}'} \xrightarrow{2\text{Na}[\text{BAr}'_4]} [\text{Pd}(\text{bipy}^{\text{R}})(\text{bipy}^{\text{R}'})][\text{BAr}'_4]_2 + 2\text{NaCl} \qquad \text{(Reaction 1)}$$

The neutral complexes $[\text{Pd}(\text{bipy}^{\text{R}})\text{Cl}_2]$ (R = Me **9**; R = Et **10**; R = *i*-Pr **11**) slightly soluble in several organic solvents, were prepared according to literature methods (see Section 4). Reaction 1 allows to obtain either species having the same (R = R′) or different bipyridines (R ≠ R′). The driving force of the second step is likely to be the insolubility of NaCl in dichloromethane.

An alternative one-pot procedure has been used in some cases to achieve symmetric species i.e. those with the same bipy ligand (reaction 2). These cationic complexes are air stable species, very soluble in most of the organic solvents, with the exception of various hydrocarbons (e.g. pentane, hexane).

$$[(\text{COD})\text{PdCl}_2] + 2\text{bipy}^{\text{R}} \xrightarrow{2\text{Na}[\text{BAr}'_4]} [\text{Pd}(\text{bipy}^{\text{R}})_2][\text{BAr}'_4]_2 + 2\text{NaCl} \qquad \text{(Reaction 2)}$$

The complexes have been characterized by elemental analyses, conductivity measurements, ^{1}H-NMR and FAB mass spectroscopy (see Section 4).

At room temperature, the ^{1}H-NMR spectra of the bis-chelated species $[\text{Pd}(\text{bipy}^{\text{R}})_2][\text{BAr}'_4]_2$ (**1**, **2**), are broad indicating a dynamic behaviour probably related to the presence of two geometric isomers arising from the lack of symmetry of the ligands. Indeed on lowering the temperature down to −50 °C, the spectrum of compound **1** becomes more sharp and evidence is achieved for two species, the minor of them likely being the less favoured of the two isomers. The spectrum of complex **3** is sharp even at room temperature.

In the FAB mass spectra (positive ions) the molecular ions $[\text{M}]^+$ at *m*/*z* 446, 474 and 502 for **1**, **2**, **3**, observed together with peaks corresponding to $[\text{M}-(\text{bipy}^{\text{R}})]^+$, provide evidence for the stability of these species even in gas phase.

Since the $[\text{PF}_6]^-$ salt of the cationic complex $[\text{Pd}(\text{bipy})_2]^{2+}$ (**8**), has been reported [2k] to be the most efficient catalytic precursor in the case of CO–styrene copolymerization, to compare the effect of the counterion, the $[\text{BAr}'_4]^-$ salt $[\text{Pd}(\text{bipy})_2][\text{BAr}'_4]_2$ (**7**), has been prepared according to reaction 1, and its activity studied in the same reaction. The structure of the yet unreported compound **7** has been solved by X-ray diffraction. An ORTEP view of the dicationic complex is shown in Fig. 1, with selected interatomic distances and angles in the figure caption. The Pd atom displays a square planar coordination with a strong tetrahedral distortion, the dihedral angle α between the Pd–N1–N2 and Pd–N3–N4 planes being 28.1(1)°. A similar distortion, with an angle α of 25.5(3)°, has been found in

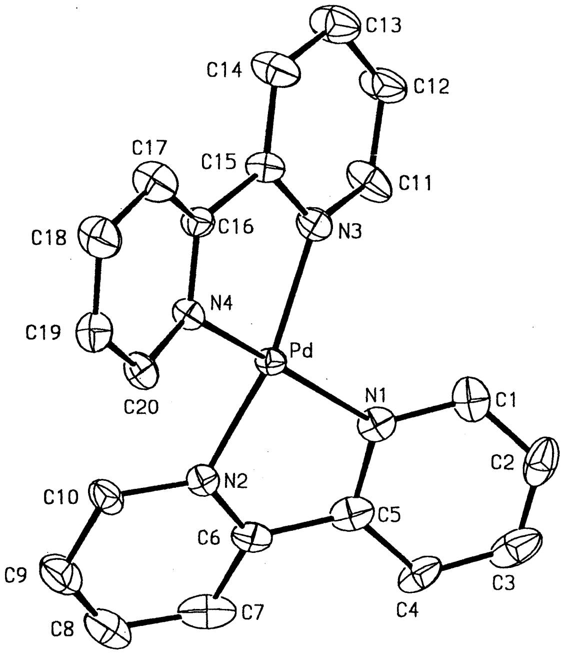


Fig. 1. ORTEP view of the cation in compound **7**. Ellipsoids are drawn at the 30% probability level. Selected bond lengths (Å) and angles (°): Pd–N(1) 2.052(3), Pd–N(2) 2.023(3), Pd–N(3) 2.023(3), Pd–N(4) 2.050(3), N(1)–Pd–N(2) 80.4(1), N(1)–Pd–N(3) 103.2(1), N(1)–Pd–N(4) 163.1(1), N(2)–Pd–N(3) 160.9(1), N(2)–Pd–N(4) 101.8(1), N(3)–Pd–N(4) 80.3(1).

$[Pd(bipy)_2][BF_4]_2$, where the resulting cation conformation has been described as *twisted* [2k]. On the contrary, in $[Pd(bipy)_2][PF_6]_2$, where the metal atom lies on a crystallographic symmetry centre, the Pd–N1–N2–N3–N4 moiety is strictly planar, and the relief from steric repulsion between the two coordinated ligands is achieved through a *bow-step* conformation, with β and γ angles of 21.6 and 19.1°, respectively (β is the dihedral angle between the Pd–N–N and the N–C–C–N best plane, and γ is the dihedral angle between the two pyridil ring best planes) [4]. In the present cation β angles are 4.0(8) and 3.5(5)° for the N1–N2 and N3–N4 ligands, respectively, whereas the corresponding γ angles are 16.8(3) and 7.9(4)°, respectively. In $[Pd(bipy)_2][BF_4]_2$ β angles are 1.0(5) and 2.0(5)°, and γ angles are 8.7(6) and 8.1(8)°. As a result, we may observe that in the present cation, besides the main *twist* distortion, there is an additional distortion in the N1–N2 ligand (γ angle of 16.8(3)°), probably due to packing forces.

Taking advantage of the second step of reaction 1, the unsymmetric derivatives $[Pd(bipy)(bipy^R)][BAr'_4]_2$ (**4**, **5**, **6**) (R = Me, Et, *i*-Pr, respectively) have been synthesized and isolated as solids which are very soluble in most common organic solvents. Evidence for the existence of these species is provided in gas-phase by the FAB mass spectra (positive ions) which show peaks corresponding to $[M]^+$. However, they are flanked by less abundant peaks at values corresponding to $[Pd(bipy)_2]^{2+}$ and $[Pd(bipy^R)_2]^{2+}$. In the fragmentation pattern, peaks due to $[M-bipy]^+$ and $[M-bipy^R]^+$ are observed in all cases. Compounds **4**–**6** are rather unstable in solution: the ^{1}H-NMR spectra (CD_3OD) show the existence of several species. The resonances, broad at room temperature, particularly in the case of complexes **4** and **5**, somewhat sharpen at low temperature (−50 °C). The aromatic region is very complex, and many signals are overlapping. Although assignment of bipy and bipy^R protons is not straightforward, careful inspection of the spectra suggests a dynamic behaviour involving bipy^R rather than bipy. The lability of substituted dinitrogen ligands in this area of palladium chemistry has been previously observed [2j]. From these results it seems that, as observed in gas-phase, both unsymmetric, $[Pd(bipy)(bipy^R)]^{2+}$ and symmetric, $[Pd(bipy^R)_2]^{2+}$ and $[Pd(bipy)_2]^{2+}$ species coexist in solution. In the complex pattern of the aromatic region only the resonances of the latter species, $[Pd(bipy)_2]^{2+}$, can be reasonably assigned. Moreover, it is worthy to note that, likely, the pattern of resonances is particularly complex owing to the possible existence of the geometrical isomers of $[Pd(bipy^R)_2]^{2+}$. In agreement with the coexistence of several species in solution in the case of unsymmetric derivatives of this type, it has been reported that attempts to grow crystals of the bis-chelated species $[Pd(bipy)(tmphen)][PF_6]_2$ failed (tmphen = 3,4,7,8-tetramethyl-1,10-phenanthroline) [4]. Indeed only crystals of $[Pd(bipy)_2][PF_6]_2$ and $[Pd(tmphen)_2][PF_6]_2$ were isolated by slow evaporation of a solution of the unsymmetric complex.

To get a better insight into the behaviour in solution of our unsymmetric complexes, we have prepared also the complexes $[Pd(bipy)(phen)][BAr'_4]_2$ (**12**) as well as $[Pd(phen)_2][BAr'_4]_2$ (**13**). The ^{1}H-NMR spectrum, in CD_3OD, of **12** shows 16 resonances, well resolved and separated, all with the same integral value, indicating that more species are present in solution. Comparison with the spectra of **7** and **13** (four well resolved resonances in each case, see Section 4), registered in the same solvent, taken together with the analysis of the remaining eight signals by means of a 2D COSY experiment, provides evidence for three species in solution, namely **7**, **13**, **12**, in a 1:1:2 molar ratio. Compounds **7** and **13** may be related by the equilibrium $2[Pd(bipy)(phen)]^{2+} \rightleftharpoons [Pd(bipy)_2]^{2+} + [Pd(phen)_2]^{2+}$ due to a scrambling of the ligands in a statistical distribution. This fact confirms the dynamic behaviour observed for the others unsymmetric derivatives.

2.1. CO–styrene and *p*-*tert*-butylstyrene copolymerization experiments

It has been reported on the effect of the counterion in the copolymerization reaction of carbon monoxide and olefins. The use of non-coordinating anions, which do not block any coordination position of the palladium precursor, leads to a better catalytic activity [1b,7]. In particular, the use of the $[BAr'_4]^-$ anion in different precursors has shown excellent results [8]. However, to the best of our knowledge, the $[BAr'_4]^-$ salts of bis-chelated precursors $[Pd(N-N)_2]^{2+}$ have not been reported.

We first explored the catalytic activity of $[Pd(bipy)_2]-[BAr'_4]_2$ in the CO–styrene copolymerization to compare with $[Pd(bipy)_2][PF_6]_2$, which has extensively been studied (Table 1) [2k,2m]. The reactions were carried out under the conditions described by Milani et al. [2k,2m], i.e. in TFE in presence of *p*-benzoquinone (BQ).

Table 1
Effect of the anion in CO–styrene copolymerization using $[Pd(bipy)_2][X]_2$ precursors

Entry	X^-	p_{CO} (atm)	g CP	g CP/(g Pd h)
1 [a]	$[PF_6]^-$	10	4.35	1083
2 [a]	$[BAr'_4]^-$	10	4.89	1215
3 [b]	$[PF_6]^-$	35	2.98	370
4 [b]	$[BAr'_4]^-$	35	3.37	419

Reaction conditions: $T = 60$ °C; $t = 14$ h; V(styrene) = 30 ml; V(TFE) = 20 ml; n(BQ) = 0.35 mmol.

[a] n(Pd) = 0.0027 mmol.

[b] n(Pd) = 0.0054 mmol.

We observed that the use of $[BAr'_4]^-$ as counterion provides a clear increase of the catalytic activity at different CO pressures and catalyst amounts. In agreement with literature, an increase of CO pressure leads to a decrease in productivity (entries 1, 2 vs. 3, 4) [2l,3a,9]. It is interesting to note that the result obtained at low pressure (entry 2) is one of the best reported for this type of precatalysts [2k].

When we further tested the 6-substituted bipyridines as ligands (in the TBS–CO copolymerization) we observed the different behaviour of the $[Pd(bipy^R)_2]$–$[BAr'_4]_2$ and $[Pd(bipy)(bipy^R)][BAr'_4]_2$ complexes (Table 2). The precursors $[Pd(bipy^R)_2][BAr'_4]_2$ (**1**, **2**, **3**) were inactive and fast decomposition to Pd metal indicated to us that the species formed under copolymerization conditions were unstable (entries 2–4). This agrees with the inactivity reported for a related in-situ system where the nitrogen ligand is 2,9-dimethyl-1,10-phenanthroline [2d]. Indeed previous studies on the reactivity of cationic Pd(II) complexes towards CO insertion reported a remarkable effect of the presence of substituents in *ortho*-position in phenanthroline ligands [10]. Likely, a sterically demanding R substituent in the *ortho*-position affects either the CO insertion or the coordination–insertion of the substrate. Previous experiments showed that the CO insertion takes place in the reaction of the $[Pd(bipy^{Me})Me(MeCN)]^+$ suggesting that probably the coordination–insertion of the substrate is disfavoured owing to the sterically demanding substituent in the *ortho*-position [11].

The activity of the bis-chelated palladium complexes containing different bis-nitrogen ligands (**4**–**6**) in the CO–TBS copolymerization reaction was tested under the same conditions, being in all the cases (entries 5–7) around half the one showed by $[Pd(bipy)_2][BAr'_4]_2$ (entry 1). These results, taken together with the presence of different cationic species in solution (see NMR spectra), seem to indicate that the active precursor contains the moiety $[Pd(bipy)]^{2+}$.

Table 2
CO–TBS copolymerization using $[Pd(N–N)(N–N')][BAr'_4]$ precursors [a]

Entry	Precursor	p_{CO} (atm)	g CP/(g Pd h)	M_n (M_w/M_n)
1	$[Pd(bipy)_2][BAr'_4]_2$	10	818	33 400 (1.50)
2	$[Pd(bipy^{Me})_2][BAr'_4]_2$	10	–	
3	$[Pd(bipy^{Et})_2][BAr'_4]_2$	10	–	
4	$[Pd(bipy^{i\text{-}Pr})_2][BAr'_4]_2$	10	–	
5	$[Pd(bipy)(bipy^{Me})][BAr'_4]_2$	10	492	n.d.
6	$[Pd(bipy)(bipy^{Et})][BAr'_4]_2$	10	471	44 800 (1.45)
7	$[Pd(bipy)(bipy^{i\text{-}Pr})][BAr'_4]_2$	10	323	44 400 (1.48)

[a] Reaction conditions: $T = 60$ °C; $t = 14$ h; V(TBS) = 10 ml; V(TFE) = 6.7 ml; n(BQ) = 4.63×10^{-3} mmol; n(Pd) = 9.26×10^{-4} mmol; n.d., not determined.

In all cases the polymeric material showed the expected resonances in the ^{13}C spectrum (see Section 4). A M_n and PDI (M_w/M_n) determination based on SEC techniques (size exclusion chromatography) was performed on the samples of entries 1, 6 and 7, showing molecular weights around 40 000.

Recently, it has been reported that the use of TFE as solvent leads to an improvement in the catalytic activity due to the higher stabilisation of the catalysts in this alcohol [2m]. Longer copolymers are obtained when TFE instead of methanol is employed as the solvent of the catalysis. The lower nucleophilicity of TFE disfavours the alcoholysis, which, in the case of methanol, is the main termination step, making the β-H-elimination the only chain-end process [2m]. In view of these results, we also performed the catalytic experiments using TFE as solvent in place of methanol and studied the influence of its amount on the activity of the precursor $[Pd(bipy)_2][BAr'_4]_2$ working at low pressure. We observed that in this case, due to the high solubility provided by the anion, the required volume of TFE could be optimized to 1 ml (Table 3).

The inactivity of the symmetric precursors $[Pd(bipy^R)_2][BAr'_4]_2$ and, in contrast, the activity, albeit modest, of $[Pd(bipy)(bipy^R)][BAr'_4]_2$ points out the remarkable role played during the catalytic process by species having an N–N ligand still chelated to the metal.

All the systems we have studied yield prevailing syndiotactic copolymers, which have alternating, head to tail, syndiotactic structure which is indicative of a chain-end stereocontrol mechanism [2b]. Analysis of the decoupled ^{13}C spectra indicated the substantial degree of stereoregularity (ca. 80%) by integration of the signals of the methylene carbon atoms. The greater resonance at 43.0 was assigned to the syndiotactic *uu*-triad by comparison with literature values [2g,2p].

2.2. ^{13}CO-NMR studies

The styrene–CO copolymerization process was monitored by $^{13}C\{^1H\}$-NMR using complex **7** as precatalyst.

Table 3
Effect of the amount of TFE using $[Pd(bipy)_2][BAr']_2$ as catalyst [a]

Entry	V(TFE) (ml)	g CP/(g Pd h)
1	0.25	1130
2	0.5	1327
3	0.75	1663
4	1.0	1684
5	2.0	1527
6	5.0	1502

[a] Reaction conditions: $T = 60$ °C; $t = 14$ h; $p_{CO} = 7.5$ atm; V(TBS) = 10 ml; n(Pd) = 5.1×10^{-4} mmol; n(BQ) = 5.1×10^{-3} mmol.

An NMR tube containing a CD_3OD solution of $[Pd(bipy)_2][BAr'_4]_2$ and styrene (molar ratio 1:10) at -60 °C was purged and pressurized to 1 atm with ^{13}CO. A first spectrum was registered at -60 °C (time 0). After that, the tube was raised from the probe, shaken to dissolve CO and a new spectrum was registered (time 1). A further series of spectra (time 2–5) was recorded; each time raising the tube and allowing the sample to undergo a temperature jump for few seconds.

Inspection of the spectrum at time 1 allowed us to assign, according to literature data, the resonance at δ 186 to free ^{13}CO (absent at time 0), and those at δ 172 and 170 to $Pd-^{13}CO$ [2c] and to the terminal $-^{13}COOCD_3$ group of the chain [12], respectively. At time 2–3 two other signals were observed at δ 206 and 218: the former may be assigned to the ketonic carbonyls of the growing chain $(CH_2-CHPh-^{13}CO-)_n$, the latter could be attributed to a palladium bonded acyl species $(Pd-^{13}CO-P)$ [2c]. The signal at δ 206 due to the ketonic carbonyls is rather broad owing to the nonequivalence of the carbonyls in a short polymeric chain. On the whole, the sequence observed agrees with the reported mechanism of copolymerization [1b]. It is worth to note, however, that in this experiment the operating conditions (-60 °C, 1 atm CO) are very different from those required in the real catalytic process.

3. Conclusions

We have prepared and characterized two series of new cationic $[Pd(N-N)_2]^{2+}$ complexes, namely $[Pd(bipy^R)_2]^{2+}$ and $[Pd(bipy)(bipy^R)]^{2+}$ (bipy = 2,2′-bypiridine, $bipy^R$ = 6-Me, 6-Et, 6-*i*-Pr-2,2′-bipyridine) as the $[BAr'_4]^-$ salts, and compared their activity in CO–styrene catalytic copolymerization with that of $[Pd(bipy)_2]^{2+}$. We have shown that: (i) the 6-substituted ligands disfavour the activity; (ii) the counterion influences the process, the $[BAr'_4]^-$ anion improving the productivity compared to $[PF_6]^-$; and (iii) the amount of TFE, used as solvent, can be optimized. Complex $[Pd(bipy)_2][BAr'_4]_2$ in the presence of TFE is shown to be one of the best catalysts, at least under 10 atm CO. The X-ray structure of this complex has been solved and compared with those of the corresponding $[BF_4]^-$ and $[PF_6]^-$ salts.

4. Experimental

4.1. General procedure

All reactions were carried out in a nitrogen atmosphere at room temperature (r.t.) using standard Schlenk techniques. Solvents were distilled and purified prior to use unless otherwise stated. The bidentate nitrogen-donor chelating ligand N^N (2,2′-bipyridine: bipy; 1,10-phenantroline: phen) were purchased from Aldrich and used as received. The salt $Na[BAr'_4]$ [13], the ligands 6-methyl-2,2′-bipyridine ($bipy^{Me}$) [5], 6-ethyl-2,2′-bipyridine ($bipy^{Et}$) [6], 6-*iso*-propyl-2,2′-bipyridine ($bipy^{i\text{-}Pr}$) [6] were synthesized according to literature procedures. The compounds $[Pd(COD)Cl_2]$, COD = 1,5-cycloctadiene, $[Pd(bipy)Cl_2]$, $[Pd(phen)Cl_2]$, $[Pd(bipy^{Me})Cl_2]$ (**7**), $[Pd(bipy^{Et})Cl_2]$ (**8**), $[Pd(bipy^{i\text{-}Pr})Cl_2]$ (**9**), were prepared by reported methods [14,15].

^1H- and ^{13}C-NMR spectra were recorded on a Varian VXR300 spectrometer with a ^1H resonance frequency of 300 MHz and on a Varian Mercury VX spectrometer with a ^1H resonance frequency of 400 MHz. Chemical shifts in ppm, are relative to TMS for ^1H and ^{13}C. Some assignments in NMR spectra were determined by $^1H-^1H$-COSY experiments. The mass spectra were obtained with a VG 7070EQ instrument operating under FAB conditions with 3-nitrobenzyl alcohol as a supporting matrix. Elemental analyses (C, H, N) were performed with a Perkin–Elmer Elemental Analyzer 240B by A. Canu (Dipartimento di Chimica, Università degli Studi di Sassari). Conductivities were measured with a Philips PW 9505 conductimeter. The molecular weight of the copolymers and molecular weight distributions were determined by gel permeation chromatography (GPC-MALLS) measurements made in THF on a Waters 510 gel-permeation chromatography device using a three-serial column system (SHODEX K80M, PLGEL MIXED-D and MIXED-E linear columns) with a Wyatt mini-DAWN Light Scattering and SHIMADZU RID-6A refractive index detector.

4.1.1. Synthesis of $[Pd(N^\wedge N)_2][BAr'_4]_2$

Method A: To a solution of $Na[BAr'_4]$ (0.30 mmol) and N^N (0.15 mmol) in 25 ml of CH_2Cl_2 was added slowly, under stirring at 20 °C, a solution of $[Pd(N^\wedge N)Cl_2]$ (0.15 mmol in 60 ml of CH_2Cl_2). The solution was let reacting for 1 h. After filtration of NaCl, the solution was evaporated to dryness in vacuum. The crude product, as pale-yellow foam, was converted to a solid by triturating with C_5H_{12} or C_6H_{14}. The analytical sample was obtained by repeated washings of the solid with the same solvents and drying for 24 h in vacuum.

Method B: To a yellow solution of $[Pd(COD)Cl_2]$ (0.5 mmol) and N^N (1 mmol) in CH_2Cl_2 (30 ml) was added under stirring, at 20 °C, solid $Na[BAr'_4]$ (1 mmol). The colour of the solution faded and a precipitate of NaCl was formed. After filtration the solution was evaporated to dryness in vacuum. The crude product, as pale-yellow foam, was converted to a solid by triturating with C_5H_{12} or C_6H_{14}. The analytical sample was obtained by repeated washings of the solid with the same solvents and drying for 24 h in vacuum.

4.1.1.1. $[Pd(bipy^{Me})_2][BAr'_4]_2$ *(**1**)*. Yield: 79%. m.p. 180–181 °C. Anal. Found: C, 47.81; H, 2.09; N, 2.66. Calc. for $C_{86}H_{44}B_2F_{48}N_4Pd$: C, 47.53; H, 2.04; N, 2.58. Λ_M (5×10^{-4} M, CH_3COCH_3) = 192 Ω^{-1} cm^2 mol^{-1}. ^{1}H-NMR (300 MHz, CD_2Cl_2, r.t.): δ 2.99 br [6H] CH_3; 7.40–8.42 [38H] aromatics; (CD_2Cl_2, −50 °C): δ 3.10 s CH_3; 7.20–8.20 aromatics (main isomer); 2.90 s CH_3; 7.20–8.40 aromatics (minor isomer). MS-FAB (*m/z*): $[M]^+$ 446, $[M-bipy^{Me}]^+$ 276, $[bipy^{Me}+H]^+$ 171.

4.1.1.2. $[Pd(bipy^{Et})_2][BAr'_4]_2$ *(**2**)*. Yield: 78%. m.p. 125–126 °C. Anal. Found: C, 47.73; H, 1.95; N, 2.30. Calc. for $C_{88}H_{48}B_2F_{48}N_4Pd$: C, 48.01; H, 2.20; N, 2.55. Λ_M (5×10^{-4} M, CH_3COCH_3) = 170 Ω^{-1} cm^2 mol^{-1}. ^{1}H-NMR (400 MHz, CD_3OD): δ 1.14 br [6H] CH_3; 2.70 br [4H] CH_2; 7.40–8.80 [38H] aromatics. MS-FAB (*m/z*): $[M]^+$ 474, $[M-bipy^{Et}]^+$ 290, $[bipy^{Et}+H]^+$ 185.

4.1.1.3. $Pd(bipy^{i\text{-}Pr})_2][BAr'_4]_2$ *(**3**)*. Yield: 53%. m.p. 73–74 °C. Anal. Found: C, 48.15; H, 2.46; N, 2.79. Calc. for $C_{90}H_{52}B_2F_{48}N_4Pd$: C, 48.49; H, 2.35; N, 2.51. Λ_M (5×10^{-4} M, CH_3COCH_3) = 188 Ω^{-1} cm^2 mol^{-1}. ^{1}H-NMR (400 MHz, CD_3OD): δ 1.40 d [12H] CH_3; 3.38 sept [2H] CH; 7.30–8.90 [38H] aromatics. MS-FAB (*m/z*): $[M]^+$ 502, $[M-bipy^{i\text{-}Pr})]^+$ 304, $[bipy^{i\text{-}Pr}+H]^+$ 199.

4.1.1.4. $[Pd(bipy)_2][BAr'_4]_2$ *(**7**)*. Yield: 74%. m.p. 139–140 °C. Anal. Found: C, 46.63; H, 1.70; N, 2.70. Calc. for $C_{84}H_{40}B_2F_{48}N_4Pd$: C, 47.03; H, 1.88; N, 2.61. Λ_M (5×10^{-4} M, CH_3COCH_3) = 190 Ω^{-1} cm^2 mol^{-1}. ^{1}H-NMR (400 MHz, CD_3OD): δ 7.63 s [24H]; 8.00 m [4H] H(5), H(5′); 8.55 td [4H] H(4), H(4′); 8.68 dd [4H] H(3), H(3′); 8.87 dd [4H] H(6), H(6′). MS-FAB (*m/z*): $[M]^+$ 418, $[M-bipy]^+$ 262, $[bipy+H]^+$ 157.

4.1.1.5. $[Pd(phen)_2][BAr'_4]_2$ *(**13**)*. Yield: 83%. m.p. 92 °C. Anal. Found: C, 47.63; H, 1.70; N, 2.70. Calc. for $C_{88}H_{40}B_2F_{48}N_4Pd$: C, 48.19; H, 1.84; N, 2.55. Λ_M (5×10^{-4} M, CH_3COCH_3) = 180 Ω^{-1} cm^2 mol^{-1}. ^{1}H-NMR (300 MHz, CD_3OD): δ 7.63 s [24H]; 8.30 dd [4H] H(3), H(8); 8.42 s [4H] H(5), H(6); 9.13 dd [4H] H(4), H(7); 9.37 dd [4H] H(2), H(9). MS-FAB (*m/z*): $[M]^+$ 466, $[M-phen]^+$ 286, $[phen+H]^+$ 181.

4.1.2. Synthesis of $[Pd(bipy)(N^\wedge N)][BAr'_4]_2$

To a solution of $Na[BAr'_4]$ (0.30 mmol) and bipy (0.15 mmol) in 25 ml of CH_2Cl_2, a solution of $[(N^\wedge N)PdCl_2]$ (0.15 mmol) in 40 ml of CH_2Cl_2 was slowly added, under stirring at r.t. The solution was left to react for 1 h. After filtration of NaCl, the solution was evaporated to dryness in vacuum. The crude product obtained as pale-yellow foam was converted to a solid by triturating with C_5H_{12} or C_6H_{14}. The analytical sample was obtained by repeated washings of the solids with the same solvents and drying for 24 h in vacuum.

4.1.2.1. $[Pd(bipy)(bipy^{Me})][BAr'_4]_2$ *(**4**)*. Yield: 80%. Anal. Found: C, 46.84; H, 1.91; N, 2.76. Calc. for $C_{85}H_{42}B_2F_{48}N_4Pd$: C, 47.28; H 1.96; N, 2.59. Λ_M (5×10^{-4} M, CH_3COCH_3) = 182 Ω^{-1} cm^2 mol^{-1}. MS-FAB (*m/z*): $[M]^+$ 432, $[Pd(bipy^{Me})_2]^+$ 446, $[Pd(bipy)_2]^+$ 418, $[M-bipy]^+$ 276, $[M-bipy^{Me}]^+$ 262, $[bipy^{Me}+H]^+$ 171, $[bipy+H]^+$ 157.

4.1.2.2. $[Pd(bipy)(bipy^{Et})][BAr'_4]_2$ *(**5**)*. Yield: 52%. Anal. Found: C, 47.45; H, 2.58; N, 2.68. Calc. for $C_{86}H_{44}B_2F_{48}N_4Pd$: C, 47.53; H, 2.04; N, 2.58. Λ_M (5×10^{-4} M, CH_3COCH_3) = 182 Ω^{-1} cm^2 mol^{-1}. MS-FAB (*m/z*): $[M]^+$ 446, $[Pd(bipy^{Et})_2]^+$ 474, $[Pd(bipy)_2]^+$ 418, $[M-bipy]^+$ 290, $[M-bipy^{Et}]^+$ 262, $[bipy^{Et}+H]^+$ 185, $[bipy+H]^+$ 157.

4.1.2.3. $[Pd(bipy)(bipy^{i\text{-}Pr})][BAr'_4]_2$ *(**6**)*. Yield: 58%. Anal. Found: C, 47.93; H, 2.50; N, 2.73. Calc. for $C_{87}H_{46}B_2F_{48}N_4Pd$: C, 47.77; H 2.12; N, 2.56. Λ_M (5×10^{-4} M, CH_3OCH_3) = 194 Ω^{-1} cm^2 mol^{-1}. MS-FAB (*m/z*): $[M]^+$ 460, $[M-bipy]^+$ 304, $[M-bipy^{i\text{-}Pr}]^+$ 262, $[bipy^{i\text{-}Pr}+H]^+$ 199, $[bipy+H]^+$ 157.

4.1.2.4. $[Pd(bipy)(phen)][BAr'_4]_2$ *(**12**)*. Yield: 85%. Anal. Found: C, 46.98; H, 2.06; N, 2.56. Calc. for $C_{86}H_{40}B_2F_{48}N_4Pd$: C, 47.62; H 1.86; N, 2.58. Λ_M (5×10^{-4} M, CH_3COCH_3) = 185 Ω^{-1} cm^2 mol^{-1}. ^{1}H-NMR (400 MHz, CD_3OD): δ 7.63 s [4 × 24H]; 8.00 (**7**) m [4H] H(5), H(5′); 8.55 (**7**) td [4H] H(4), H(4′); 8.68 (**7**) dd [4H] H(3), H(3′); 8.87 (**7**) dd [4H] H(6), H(6′); 8.33 (**13**) dd [4H] H(3), H(8); 8.42 (**13**) s [4H] H(5), H(6); 9.15 (**13**) dd [4H] H(4), H(7); 9.37 (**13**) dd [4H] H(2), H(9); 9.26 (**12**) dd [4H] H(2), H(9); 9.12 (**12**) dd [4H] H(4), H(7); 8.97 (**12**) dd [4H] H(6), H(6′); 8.72 (**12**) dd [4H] H(3), H(3′); 8.56 (**12**) td [4H] H(4), H(4′); 8.37 (**12**) s [4H] H(5), H(6); 8.29 (**12**) dd [4H] H(3), H(8); 8.03 (**12**) m [4H] H(5), H(5′).

4.2. Copolymerization reactions—general procedure

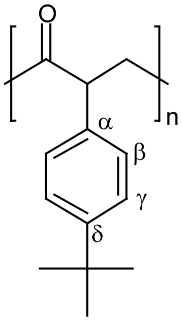
Styrene and TBS (Aldrich) were passed through a small column of basic Al_2O_3 prior to use. 2,2,2-Trifluorethanol, 1,4-benzoquinone (BQ) were purchased from Aldrich and used as received.

The reactions were carried out in a stainless steel autoclave (150 ml), equipped with a magnetic stirrer and a temperature controller. The precursor, styrene or 4-*tert*-butylstyrene, 1,4-benzoquinone and the alcohol were placed in the autoclave, which was purged, then pressurized with CO and heated. After cooling and releasing the residual gas, the solution was poured dropwise into 200 ml of stirring MeOH. The white precipitate was collected by filtration, washed with MeOH and dried in a vacuum oven at 70 °C overnight.

4.2.1. Copolymer CO–TBS characterization

^{1}H-NMR (300 MHz, $CDCl_3$, r.t.): δ 7.0 (d $^3J = 8.1$ Hz), 2H H_β or H_γ; 6.6 (d $^3J = 8.1$ Hz), 2H H_γ or H_β; 4.11 (t $^3J = 7.1$ Hz), 1H (CH); 3.0 (dd $^2J = 18.1$, $^3J = 6.8$ Hz), 1H (CH_2); 2.6 (dd $^2J = 18.1$, $^3J = 6.8$ Hz), 1H (CH_2); 1.23 (s, 9H, $C(CH_3)_3$).

^{13}C-NMR (75.4 MHz, $CDCl_3$, r.t.): δ 206.7 (–C(O)–); 149.6 (C_δ); 134.0 (C_α); 128.0 (C_γ); 125.4 (C_β); 52.6 (CH); 43.0 (CH_2); 34.3 ($C(CH_3)_3$); 31.3 ($C(CH_3)_3$).



4.3. ^{13}CO-NMR study

The spectroscopic study on the mechanism has been carried out charging an NMR tube with 10.0 mg of $[Pd(bipy)_2][BAr'_4]$ (4.66×10^{-3} mmol), 5.5 µl of styrene (4.6×10^{-2} mmol) and MeOH-d_4 as solvent. The ^{13}CO (1 atm) has been charged after cooling the tube with a cooling bath (C_3H_6O–liquid nitrogen). All NMR spectra have been registered at −60 °C. After the registration of the first spectrum the NMR tube was extracted from the probe and slightly shaked to help the CO diffusion. After the registration of the 1, 2, 3 and 4th spectra the NMR tube was extracted from the probe for few seconds allowing the sample to react faster.

Table 4
Crystallographic data

Compound	**7**
Empirical formula	$C_{84}H_{40}B_2F_{48}N_4Pd$
M	2145.23
T (K)	200
Colour	Bright yellow
Crystal system	Triclinic
Space group	$P\bar{1}$ (No. 2)
a (Å)	13.575(1)
b (Å)	15.342(1)
c (Å)	21.709(2)
α (Å)	84.58(1)
β (Å)	87.30(1)
γ (Å)	80.85(1)
U (Å^3)	4441.4(8)
Z	2
$F(000)$	2120
D_{calc} (g cm^{-3})	1.60
μ(Mo–K_α) (cm^{-1})	3.48
Crystal dimensions (mm)	0.16 × 0.28 × 0.29
θ Range (°)	3–26
Min/max transmission factors	0.86–1.00
Scan mode	ω
Frame width (°)	0.30
Time per frame (s)	35
Frames	1868
Detector-sample distance (cm)	5.00
Reciprocal space explored	Full sphere
Reflections (total; independent)	55 189; 26 173
R_{int}	0.040
Final R_2 and wR_2 indices [a] (F^2, all reflections)	0.113, 0.159
Conventional R_1 index [$I > 2\sigma(I)$]	0.063
Reflections with $I > 2\sigma(I)$	14 864
Variables	1306
Goodness-of-fit [b]	1.17

[a] $R_2 = [\Sigma\,(|F_o^2 - kF_c^2|)/\Sigma\,F_o^2]$, $wR_2 = [\Sigma\,w(F_o^2 - kF_c^2)^2/\Sigma\,w(F_o^2)^2]^{1/2}$.

[b] $[\Sigma\,w(F_o^2 - kF_c^2)^2/(N_o - N_v)]^{1/2}$, where $w = 4F_o^2/\sigma(F_o^2)^2$, $\sigma(F_o^2) = [\sigma^2(F_o^2) + (0.04F_o^2)^2]^{1/2}$, N_o is the number of observations and N_v the number of variables.

4.4. X-ray data collection and structure determination

Crystal data and other experimental details are summarized in Table 4. The diffraction experiment was carried out on a Bruker SMART CCD area-detector diffractometer at 200 K using Mo–K_α radiation ($\lambda = 0.71073$ Å) with a graphite crystal monochromator in the incident beam. Cell parameters and orientation matrix were obtained from the least-squares refinement of 113 reflections measured in three different sets of 15 frames each, in the range $3 < \theta < 23°$. At the end of data collection the first 50 frames, containing 231 reflections, were recollected to have a monitoring of crystal decay, which was not observed, so that no time-decay correction was needed. The collected frames were processed with the software SAINT [16a], and an absorption correction was applied (SADABS) [16b] to the 55 189 collected reflections [26 173 of which are unique with $R_{int} = 0.0404$ ($R_{int} = \Sigma\,|F_o^2 - F_{mean}^2|/\Sigma\,F_o^2$)].

The calculations were performed on a Pentium III Pc using the Personal Structure Determination Package [17] and the physical constants tabulated therein. Scattering factors and anomalous dispersion corrections were taken from Ref. [18]. The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares using all reflections and minimizing the function $\Sigma\,w(F_o^2 - kF_c^2)^2$ (refinement on F^2). Anisotropic thermal factors were refined for all the non-hydrogen atoms. The hydrogen atoms were placed in their ideal positions (C–H = 0.97 Å, B 1.10 times that of the carbon atom to which they are attached) and not refined. In the $[B(3,5\text{-}(CF_3)_2C_6H_3)_4]^-$ anions many (but not all) CF_3 groups are affected by rotational disorder about the C–C(F_3) linkages to the C6 ring. In two CF_3

groups two preferred positions could be assigned to the F atoms, which were refined with occupancy factors of 0.50 each. In all the other cases there was a clearly prevailing position for each F atom, and this was refined with occupancy factor of 1.00 and anisotropic thermal factor. In the final difference Fourier map the maximum residual was 1.52(24) e Å^{-3} at 0.56 Å from Pd.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 182370 for compound **7**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

We thank the Università di Sassari and the Spanish Ministerio de Education, Cultura y Deporte (DGES PB-97-0407-C05-01 and DGES I+D, FEDER, 2FD97-1565) for financial support; the Ministerio de Ciencia y Tecnologia for awarding a research grant (to A.B.) We are also much indebted to Ramòn Guerrero (Servei de Recursos Cientifics, Universitat Rovira i Virgili) for carrying out the ^{13}CO-NMR studies.

References

[1] (a) A. Sen, Acc. Chem. Res. 26 (1993) 303;
(b) E. Drent, P.H.M. Budzelaar, Chem. Rev. 96 (1996) 663;
(c) C. Bianchini, A. Meli, Coord. Chem. Rev. 225 (2002) 35;
(d) E. Drent, Eur. Pat. Appl. 229, 408, 1986.;
(e) P. Corradini, A. De Rosa, A. Panunzi, P. Pino, Chimia 44 (1990) 52;
(f) M. Barsacchi, G. Consiglio, L. Medici, G. Petrucci, U.W. Suter, Angew. Chem. 103 (1991) 992; Angew Chem. Int. Ed. Engl. 30 (1991) 989.;
(g) V. Busico, P. Corradini, L. Landriani, M. Trifuoggi, Macromol. Chem. Rapid Commun. 14 (1993) 261;
(h) B. Milani, G. Mestroni, Comments Inorg. Chem. 20 (1999) 301.

[2] (a) C. Pisano, S.C.A. Nefkens, G. Consiglio, Organometallics 11 (1992) 1975;
(b) C. Pisano, C. Mezzetti, G. Consiglio, Organometallics 11 (1992) 20;
(c) M. Brookhart, F. Rix, J.M. De Simone, J.C. Barborak, J. Am. Chem. Soc. 114 (1992) 5894;
(d) A. Sen, Z. Jiang, Macromolecules 26 (1993) 911;
(e) J. Zhaozhong, S.E. Adam, A. Sen, Macromolecules 27 (1994) 2694;
(f) C. Pisano, G. Consiglio, Gazz. Chim. It. 124 (1994) 393;
(g) M. Brookhart, M.I. Wagner, G.G.A. Balavoine, H.A. Haddou, J. Am. Chem. Soc. 116 (1994) 3641;
(h) B. Milani, E. Alessio, G. Mestroni, A. Sommazzi, F. Garbassi, E. Zangrando, N. Bresciani-Pahor, L. Randaccio, J. Chem. Soc. Dalton Trans. 13 (1994) 1903;
(i) S. Bartolini, C. Carfagna, A. Musco, Macromol. Chem. Rapid. Commun. 16 (1995) 9;
(j) M. Brookhart, M.I. Wagner, J. Am. Chem. Soc. 118 (1996) 7219;
(k) B. Milani, A. Anzilutti, L. Vicentini, A. Sessanta o Santi, E. Zangrando, S. Geremia, G. Mestroni, Organometallics 16 (1997) 5064;
(l) A. Aeby, G. Consiglio, Inorg. Chim. Acta 45 (1999) 296;
(m) B. Milani, G. Corso, G. Mestroni, C. Carfagna, M. Formica, R. Seraglia, Organometallics 19 (2000) 3435;
(n) M.T. Reetz, G. Haderlein, K. Angermund, J. Am. Chem. Soc. 122 (2000) 996;
(o) C. Carfagna, G. Gatti, D. Martini, C. Pettinari, Organometallics 20 (2001) 2175;
(p) A. Bastero, A. Ruiz, J.A. Reina, C. Claver, A.M. Guerrero, F.A. Jalón, B.R. Manzano, J. Organomet. Chem. 619 (2001) 287.

[3] (a) B. Milani, E. Alessio, G. Mestroni, E. Zangrando, L. Randaccio, G. Consiglio, J. Chem. Soc. Dalton Trans. (1996) 1021;
(b) R. Santi, A.M. Romano, R. Garrone, L. Abbondanza, M. Scalabrini, G. Bacchilega, Macromol. Chem. Phys. 200 (1999) 25;
(c) A. Bastero, A. Ruiz, C. Claver, S. Castillón, Eur. J. Inorg. Chem. 12 (2001) 3009;
(d) B. Milani, A. Scarel, G. Mestroni, S. Gladiali, R. Taras, C. Carfagna, L. Mosca, Organometallics 21 (2002) 1323.

[4] S. Geremia, L. Randaccio, G. Mestroni, B. Milani, J. Chem. Soc. Dalton Trans. (1992) 2117.

[5] For bipy^R, R = Me: T. Kaussmann, J. Konig, A. Woltermann, Chem. Ber. 109 (1976) 3864.

[6] For bipy^R, R = Et, *i*-Pr: (a) C. Botteghi, G. Chelucci, M. Marchetti, Synth. Commun. 12 (1982) 25;
(b) U. Azzena, G. Chelucci, G. Delogu, S. Gladiali, M. Marchetti, F. Soccolini, C. Botteghi, Gazz. Chim. Ital. 116 (1986) 307;
(c) C. Botteghi, G. Chelucci, G. Chessa, G. Delogu, S. Gladiali, F. Soccolini J. Organomet. Chem. 304 (1986) 217.

[7] K. Nozaki, T. Hiyama, J. Organomet. Chem. 576 (1999) 248.

[8] A. Macchioni, G. Bellachioma, G. Cardaci, M. Travaglia, C. Zuccaccia, B. Milani, G. Corso, E. Zangrando, G. Mestroni, C. Carfagna, M. Formica, Organometallics 18 (1999) 3061.

[9] F.C. Rix, M. Brookhart, P.S. White, J. Am. Chem. Soc. 118 (1996) 4746.

[10] J.H. Groen, B.J. de Jong, J.M. Ernsting, P.W.N.M. van Leeuwen, K. Vrieze, W.J.J. Smeets, A.L. Spek, J. Organomet. Chem. 573 (1999) 3.

[11] S. Deledda, Thesis, University of Sassari, 1999.

[12] R. Goddard, M. Green, R.P. Hughes, P. Woodward, J. Chem. Soc. Dalton Trans. (1992) 1890.

[13] M. Brookhart, B. Grant, A.F. Volpe, Organometallics 11 (1992) 3920.

[14] J. Chatt, L.M. Vallarino, L.M. Venanzi, J. Chem. Soc. (1957) 3413.

[15] A. Zucca, M.A. Cinellu, M.V. Pinna, S. Stoccoro, G. Minghetti, M. Manassero, M. Sansoni, Organometallics 19 (2000) 4295.

[16] (a) SAINT Reference Manual, Siemens Energy and Automation, Madison, WI, 1994–1996;
(b) G.M. Sheldrick, SADABS, Empirical Absorption Correction Program, University of Göttingen, 1997.

[17] (a) B.A. Frenz, Comput. Phys. 2 (1988) 42;
(b) B.A. Frenz, Crystallographic Computing 5 (Chapter 11), Oxford University Press, Oxford, UK, 1991, p. 126.

[18] International Tables for X-ray Crystallography, vol. 4, Kynoch Press, Birmingham, 1974.