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The role of ancillary ligands and of electron poor alkenes and alkynes in stabilizing Pd(0) derivatives: A comparative study

Luciano Canovese [a,*], Fabiano Visentin [a], Claudio Santo [a], Alessandro Dolmella [b]

[a] Dipartimento di Chimica, Università Ca' Foscari di Venezia, 30129 Venice, Italy
[b] Dipartimento di Scienze Farmaceutiche, Università di Padova, Padua, Italy

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ABSTRACT

The peculiar characteristics of the ligand neocuproine (2,9-dimethylphenanthroline) allow a number of exchange equilibrium studies between the low valence complex [Pd(η^2-nq)(Neocup)] (nq = naphthoquinone; Neocup = neocuproine) and several alkenes and alkynes. A new order of stability which compares differently unsaturated molecules was established. An overview of the factors governing the stability of palladium(0) alkene and alkyne derivatives as a function of the steric and electronic characteristics of both the unsaturated molecule and the ligand becomes accessible and a comparison with the previously determined order was therefore feasible. Such a comparison enlightens the importance of the substituent methyl groups in *ortho* position of the hetero-aromatic ring which represents the molecular fragment common to all the ligands considered. Taking advantage of the steric requirements of the alkene tmetc (tmetc = tetramethylethylenetetracarboxylate) a kinetic investigation of the reaction between the olefin itself and the complexes [Pd(η^2-dmfu)(L-L′)] (dmfu = dimethylfumarate; L–L′ = 8-diphenylphosphanyl-2-methyl-quinoline, neocuproine, phenanthroline) was carried out. The structures of the complexes [Pd(η^2-dmfu)(DPPQ)] and [Pd(η^2-deta)(Neocup)] (deta = but-2-ynedioc acid diethyl ester) were also reported in the present paper. The structure of the latter represents the first example of a palladium(0) complex in which the N_2C_2 donor set around the metal centre is supported by a chelating η^2-alkyne.

1. Introduction

Owing to the great importance of palladium(0) olefin derivatives in catalysing cross-coupling [1], allyl alkylation [2], allyl amination [3] reactions and processes involving unsaturated molecules [4] we decided to carry out an exhaustive study with the aim of gaining a better comprehension of the stability of such complexes as a function of the nature of the olefin, alkyne (when possible) and ancillary ligand. Several papers have appeared in the literature dealing with the stability that deactivated olefins impart to the corresponding palladium(0) derivatives [5] and, in particular, our group determined in some cases a stability order based on the equilibrium constant of the direct exchange between olefins according to the following reaction [6a,6b]:

$$[Pd(\eta^2\text{-ol}_1)(\text{L-L}')] + \text{ol}_2 \rightleftharpoons [Pd(\eta^2\text{-ol}_1)(\text{L-L}')] + \text{ol}_1. \quad (1)$$

The previous studies, however, took into account reactions involving complexes bearing strictly homogenous series of ligands; thus only the mutual olefin stability order could be assessed [6]. However, some recent findings about the reactivity of the olefins when used as stabilizing molecules in reactions producing palladium(0) substrates [7] and the possibility of expanding the stability order also to the alkynes induced us to undertake a novel investigation using a palladium(0) species bearing the neocuproine ligand (Neocup) as a reference. As a matter of fact, it is well known that steric hindrance may stabilize the formation of palladium(0) alkyne species [8] which in the presence of an excess of alkyne otherwise collapse into the palladacyclopentadienyl derivatives [4p,4t]. Therefore, the complex [Pd(η^2-nq)(Neocup)] (nq = naphthoquinone) would represent an ideal substrate for a useful comparison of the stability induced by olefins or alkynes in palladium(0) complexes. Moreover, the olefin nq due to its spectroscopic characteristics was widely used in the equilibrium constants measured so far. Thus, a comparative analysis among different complexes bearing different ligands and the same olefin becomes feasible. Moreover, the ensuing results would also give an indication of the dependence of the stability order on the nature of the ancillary ligands. At the best of our knowledge, this sort of investigation represents a quite novel approach which was never exploited before. All the complexes and the olefins (or alkynes) involved in the present work are reported in the following Schemes. In particular, Scheme 1 displays the newly prepared complexes and those used for comparative purposes, while in Scheme 2 only the complexes specifically synthesized for this study are reported.

* Corresponding author. Tel.: +39 041 2348571; fax: +39 041 2348517.
E-mail address: cano@unive.it (L. Canovese).

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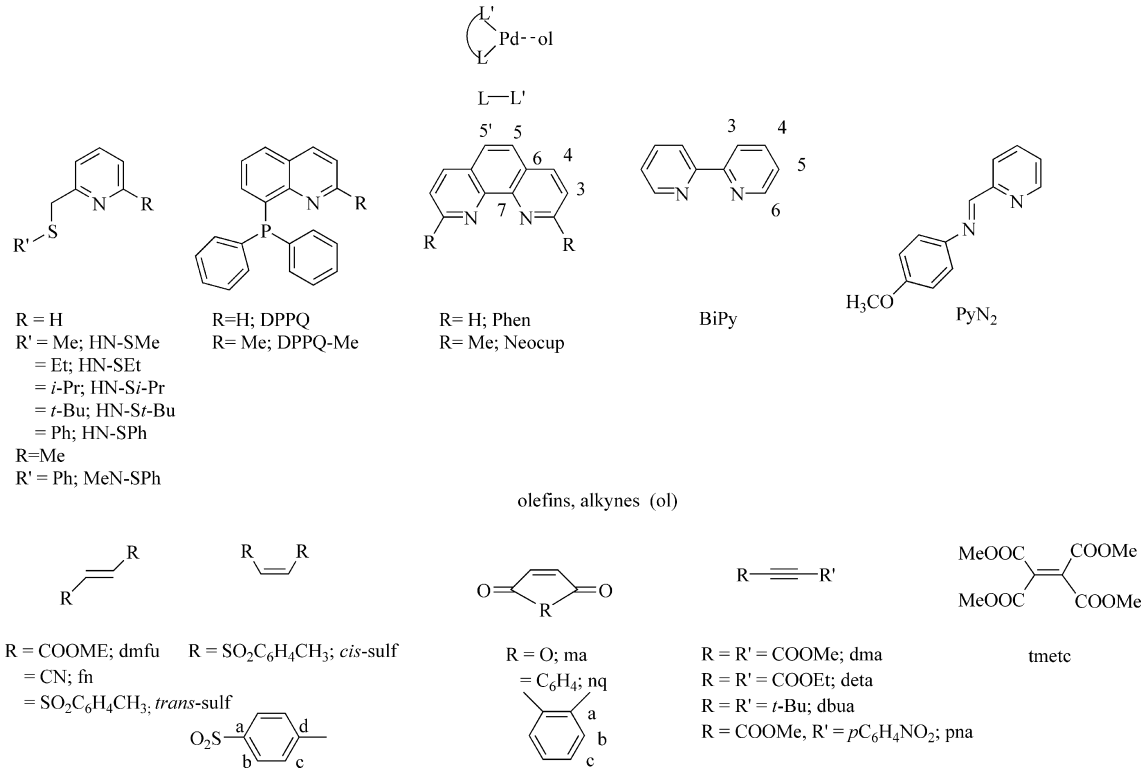
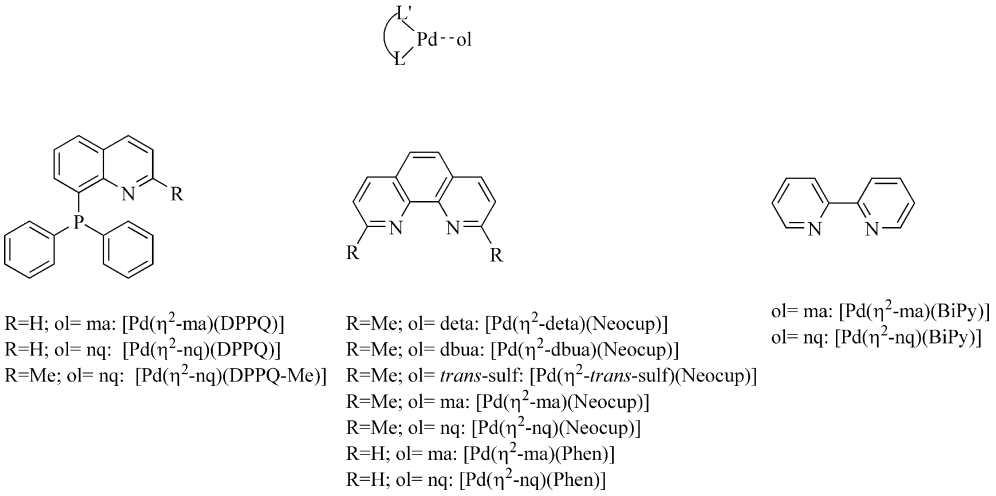


Scheme 1.



Scheme 2.

2. Results and discussion

2.1. Synthesis and characterization of palladium(0) complexes

The palladium(0) alkene and alkyne derivatives were usually obtained by reacting the appropriate ligand (L-L′) and olefin (ol) with $Pd_2DBA_3 \cdot CHCl_3$ dissolved in anhydrous acetone under inert atmosphere (Ar). The palladium(0) complexes bearing Phen, Neocup and BiPy as ancillary ligand and ma or nq as stabilizing olefin were obtained by reacting the appropriate dmfu derivatives with the specific olefin because their low solubility makes the work-up of standard procedure very difficult.

In the ^1H and ^{13}C NMR spectra of the olefin complexes, the resonances ascribable to the alkene protons and carbons when compared with the signals of the free olefins are shifted upfield (2–3 and 80–90 ppm, respectively). In the ^{13}C NMR spectra of the alkyne–palladium complexes, the alkyne carbon resonances appear at lower frequency (approximately 35 ppm) compared with those of the free molecules. These findings testify the strong metal to alkene and metal to alkyne π back donation which is also reflected by the lower frequency shifts of the alkenic and alkynic $\nu_{C=O}$ bands in the IR spectra. The chemical shifts of the sp carbons of the three coordinated alkynes ([Pd(η²-dma)(Neocup)], [Pd(η²-deta)(Neocup)], [Pd(η²-dbua)(Neocup)]) appear not to be influenced by the nature of the alkynes themselves (δ_v values span within 1 ppm). Similar behaviour can be found when the chemical shifts of the sp^2 carbons in *cis* or *trans* olefins are compared ([Pd(η²-*cis*-sulf)(Neocup)], [Pd(η²-*trans*-sulf)(Neocup)]) irrespectively of the

large differences among the formation equilibrium constants. This fact also testifies the scarce influence of the nature of the alkene or alkyne on the NMR parameters when series of homogeneous compounds are taken into consideration [9]. Conversely the coordination of the ancillary ligands is shown by a general, but less significant downfield shift of all their signals, indicating that σ donation is predominant in the palladium–ligand bond.

At variance with the RN-SR [6b] and PyN_2 [6a] derivatives the complexes bearing the ligands Phen, Neocup, BiPy and DPPQ do not show fluxional rearrangements in solution at 298 K.

2.2. X-ray crystal structure

The crystal structures of the complexes [Pd(η²-dmfu)(DPPQ)] and [Pd(η²-deta)(Neocup)] are shown in Fig. 1, whereas selected bond lengths and angles of the two molecules are listed in Table 1.

It is worth noting here that despite the large number of reported Pd structures there are only ten mononuclear square planar Pd complexes showing a coordinated η²-alkyne. In these cases the other coordination positions are held by a chelating diphosphine and thus the donor set is P_2C_2. Similarly, only five mononuclear square planar Pd complexes show the metal chelated by a phenanthroline-like moiety and by a chelating olefin defining the N_2C_2 donor set [10b]. Accordingly, to the best of our knowledge, the complex [Pd(η²-deta)(Neocup)] presented here turns out to be the first reported example in which the N_2C_2 donor set around Palladium is supported by a coordinated η²-alkyne. In this neutral complex the Pd(0) atom lies at the centre of an almost regular square planar and its averaged Pd–C bond length displays a noticeable shortening if compared with those determined when diphosphine ligands are employed (2.001 versus 2.051 Å) [10b]. The lower *trans*-influence of the neocuproine nitrogen with respect to that of phosphorus atom is apparent also when complexes of palladium(0) are considered.

In [Pd(η²-dmfu)(DPPQ)] the atoms in the main coordination plane (N, P, C(22), C(23)) and Pd are coplanar within 0.01 Å; in [Pd(η²-deta)(Neocup)] the atoms N(1), N(2), C(1), C(5) are coplanar within 0.02 Å and Pd is off by 0.06 Å. The dihedral angle between the planes N–Pd–P and C(22)–Pd–C(23) is 1.0°, the corresponding one between N(1)–Pd–N(2) and C(1)–Pd–C(5) is 4.6°.

The C–C distances of the coordinated olefin/alkyne in the two complexes fit with known data and reflect the double bond/triple bond nature of the link. In [Pd(η²-dmfu)(DPPQ)], the C(22)–C(23) distance is 1.426(5) Å, very close to the average of 1.427 Å found in 51 tetracoordinated complexes in which Pd is bound to an acyl-substituted olefin. In [Pd(η²-deta)(Neocup)], the C(1)–C(5) bond is 1.280(5) Å, at the upper end of the range found in the literature [10b].

Table 1
Selected bond lengths (Å) and angles (deg) for the complexes [Pd(η²-dmfu)(DPPQ)] and [Pd(η²-deta)(Neocup)].

[Pd(η²-dmfu)(DPPQ)]			[Pd(η²-deta)(Neocup)]		
Pd–N	2.156	(3)	Pd–N(1)	2.153	(3)
Pd–P	2.266	(1)	Pd–N(2)	2.149	(3)
Pd–C(22)	2.066	(3)	Pd–C(1)	2.006	(4)
Pd–C(23)	2.112	(3)	Pd–C(5)	1.996	(4)
C(22)–C(23)	1.426	(5)	C(1)–C(5)	1.280	(5)
N–Pd–P	83.2	(1)	N(1)–Pd–N(2)	77.8	(1)
N–Pd–C(22)	156.8	(1)	N(1)–Pd–C(1)	158.1	(1)
N–Pd–C(23)	116.9	(1)	N(1)–Pd–C(5)	120.9	(1)
P–Pd–C(22)	120.0	(1)	N(2)–Pd–C(1)	123.8	(1)
P–Pd–C(23)	159.9	(1)	N(2)–Pd–C(5)	160.7	(1)
C(22)–Pd–C(23)	39.9	(1)	C(1)–Pd–C(5)	37.3	(1)

In both complexes the polycyclic chelating ligand forms a five-membered ring showing an envelope (C_s) conformation. The involved atoms other than Pd in [Pd(η²-dmfu)(DPPQ)] are P, C(7), C(8), N, while in [Pd(η²-deta)(Neocup)] they are N(2), C(19), C(20), N(1). In the former complex the Pd atom is off plane by 0.37 Å and torsion angles in the ring range from −11.3° to +13.8°, in the latter the Pd atom deviates by 0.27 Å and torsion angles in the ring vary from −9.4° to +9.1°. As for the overall geometry, in [Pd(η²-dmfu)(DPPQ)] the main coordination plane makes dihedral angles of 15.3° with the mean plane of the quinoline moiety and of 7.1° with the average five-membered ring plane. In [Pd(η²-deta)(Neocup)] the corresponding angles are of 11.5° with the mean plane of neocuproine and of 6.4° with the average five-membered ring plane.

2.3. Determination of the equilibrium constants

All the equilibrium constants related to reaction (1) were preliminarily studied by ^{1}H NMR technique in $CDCl_3$ and then determined by recording the UV–Vis spectral changes in the range 300–600 nm obtained upon addition of the titrant alkene (or alkyne) to the complex solution in $CHCl_3$ at 298 K. In any case, the equilibrium was rapidly established and the ensuing absorbance versus olefin concentration data were analyzed at suitable wavelength by means of a non-linear least-squares program according to the model (in some cases where K_E was large an excess of free ol_1 had to be added to balance the equilibrium position):

$$K_E = [[Pd(\eta^2\text{-}ol_2)(L\text{-}L')]] \cdot [ol_1]/[[Pd(\eta^2\text{-}ol_1)(L\text{-}L')]] \cdot [ol_2],$$
$$[Pd]_0 = [[Pd(\eta^2\text{-}ol)_2)(L\text{-}L')]] + [[Pd(\eta^2\text{-}ol_1)(L\text{-}L')]],$$
$$[ol_1] + [ol_2] = [ol_1]_0 + [ol_2]_0,$$
$$[ol_1] = [ol_1]_0 + [[Pd(\eta^2\text{-}ol_2)(L\text{-}L')]],$$
$$D_\lambda = \varepsilon_1 \cdot [[Pd(\eta^2\text{-}ol_1)(L\text{-}L')]] + \varepsilon_2 \cdot [[Pd(\eta^2\text{-}ol_2)(L\text{-}L')]],$$

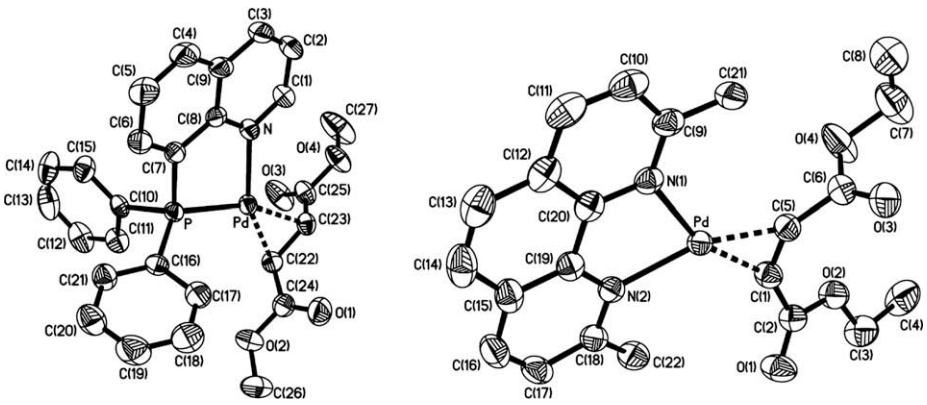


Fig. 1. Ortep [10a] views of the complexes [Pd(η²-dmfu)(DPPQ)] (left) and [Pd(η²-deta)(Neocup)] (right), together with the numbering scheme. Pd–C bonds are shown as dashed lines. Thermal ellipsoids at the 40% probability level; hydrogen atoms not shown for clarity.

where ε_1 and ε_2 are the extinction coefficients of the complexes [Pd(η^2-ol$_1$)(L-L′)] and [Pd(η^2-ol$_2$)(L-L′)], respectively, with K_E and ε_2 as the parameters to be optimized. The latter parameter (ε_2) turned out to be coincident with that directly determined from the Lambert–Beer analysis carried out at the same wavelength for the independently synthesized final product (Fig. 2).

All the K_E values directly determined in this study (apart from four values included for reasons of convenience) are reported in Table 2.

As can be seen the alkynes dma, deta, dbua and pna are included in Table 2 since the peculiar structure of Neocup stabilizes the monoalkyne palladium(0) derivative which otherwise would add a further alkyne molecule to give a palladium(II) cyclopentadienyl derivative [4t and references therein].

2.4. New neocuproine based stabilizing order

Taking advantage of such particular behaviour, we are now able to propose a new and wider order in which the stabilizing characters of some olefins and alkynes are directly compared for the first time (Table 3):

From these values it is possible to infer that:

(a) In the case of the already studied alkenes the coordinating capability order parallels those previously determined (dmfu ≪ nq < fn ⩽ ma) [6a,6b].
(b) The *trans*-sulf, the *cis*-sulf and the alkynes represent quite new entries in the molecular set establishing the stability order of the palladium(0) derivatives (items 1, 3, 5, 6, 7, 10).
(c) The same substituent (COOMe) imparts a different stabilizing property to its alkene or alkyne derivative. The alkyne dma is more efficient than the alkene dmfu (items 2, 6).
(d) The stability of the complex bearing *trans*-sulf is considerably higher than that of the complex bearing *cis*-sulf (items 10, 7).
(e) The stability range of the structurally similar *trans* olefins is modulated by the nature of the substituents according to the following order: SO_2 > CN > $COOCH_3$ (items 10, 8, 2).
(f) The steric hindrance of the alkynes is of paramount importance in determining the equilibrium constant values (items 3, 5, 6).
(g) The COOMe group displays a greater capability in stabilizing the palladium(0) derivatives than the -$C_6H_4NO_2$-4 moiety (items 1, 6).

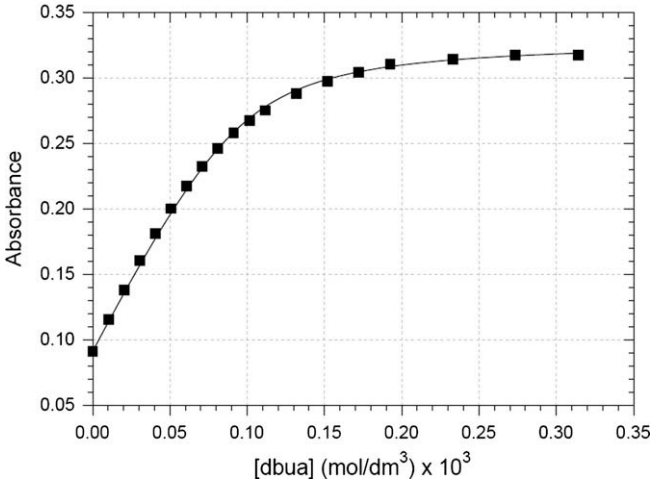


Fig. 2. Fit of absorbance versus [dbua] at 298 K and 425 nm for the reaction:[Pd(η^2-dmfu)(Neocup)] + dbua⇆[Pd(η^2-dbua)(Neocup)] + dmfu.

Table 2
Olefin exchange equilibrium constants directly determined for the reactions.

[Pd(η^2-ol$_1$)(L-L′)]	ol$_2$	K_E
[Pd(η^2-nq)(Neocup)]	dbua	0.018 ± 0.003
[Pd(η^2-nq)(Neocup)]	fn	310 ± 50
[Pd(η^2-nq)(Neocup)]	ma	630 ± 180
[Pd(η^2-fn)(Neocup)]	deta	0.0088 ± 0.0022
[Pd(η^2-fn)(Neocup)]	*cis*-sulf	0.20 ± 0.04
[Pd(η^2-fn)(Neocup)]	*trans*-sulf	15 ± 5
[Pd(η^2-fn)(Neocup)]	dma	0.0122 ± 0.0006 [4t]
[Pd(η^2-dmfu)(Neocup)]	pna	0.236 ± 0.004 [7a]
[Pd(η^2-dmfu)(Neocup)]	dbua	57 ± 4
[Pd(η^2-nq)(DPPQ)]	fn	1.4 ± 0.3
[Pd(η^2-nq)(DPPQ)]	ma	4.5 ± 0.4
[Pd(η^2-dmfu)(DPPQ)]	fn	4600 ± 600 [9]
[Pd(η^2-fn)(DPPQ)]	*cis*-sulf	270 ± 50 [9]
[Pd(η^2-dmfu)(DPPQ-Me)]	nq	2600 ± 800
[Pd(η^2-nq)(DPPQ-Me)]	fn	12 ± 3.6
[Pd(η^2-nq)(DPPQ-Me)]	ma	38 ± 17
[Pd(η^2-nq)(Phen)]	fn	3.9 ± 0.7
[Pd(η^2-nq)(Phen)]	ma	10.7 ± 0.6
[Pd(η^2-nq)(BiPy)]	fn	2.5 ± 0.2
[Pd(η^2-dmfu)(BiPy)]	nq	5600 ± 1600
[Pd(η^2-dma)(BiPy)]	ma	4.8 ± 0.5

[Pd(η^2-ol$_1$)(Neocup)] + ol$_2$ ⇌ [Pd(η^2-ol$_2$)(Neocup)] + ol$_1$.
[Pd(η^2-ol$_1$)(Neocup)] + alkyne ⇌ [Pd(η^2-alkyne)(Neocup)] + ol$_1$.

Table 3
Alkene or alkyne exchange equilibrium constants directly determined or calculated as a combination of the directly measured K_E values (Table 2), for the reactions.

	ol$_2$/alkyne	K_E
1	pna	0.000082 ± 0.000001
2	dmfu	0.00032 ± 0.00002
3	dbua	0.018 ± 0.003
4	nq	1
5	deta	2.7 ± 0.7
6	dma	3.8 ± 0.6
7	*cis*-sulf	62 ± 16
8	fn	310 ± 50
9	ma	630 ± 180
10	*trans*-sulf	4650 ± 1700

[Pd(η^2-nq)(Neocup)] + ol$_2$ ⇌ [Pd(η^2-ol$_2$)(Neocup)] + nq.
[Pd(η^2-nq)(Neocup)] + alkyne ⇌ [Pd(η^2-alkyne)(Neocup)] + nq.

As can be deduced from Table 3, the coordinating capability of the alkynes deta and dma is similar to that of nq which represents our reference, while dbua and pna are about two and three orders of magnitude less stabilizing than nq, respectively. As for point (c) it is noteworthy that the same substituent (COOMe) imparts to the alkyne dma a stabilizing efficiency of about four orders of magnitude higher than that of the alkene dmfu. Apparently, the higher electron withdrawing character of the alkyne as compared with that of the corresponding alkene favours a larger electron back-donation from the palladium(0) centre. Point (d) consists of an observation based on a unique experimental datum. Such an observation, however, probably represents a general trend due to the fact that the intrinsic higher thermodynamic stability of the *trans* olefin when compared with that of the *cis* one is somehow transferred to its corresponding palladium(0) derivative. For instance, the authors were never able to obtain a palladium(0) complex bearing dimethyl-maleate as stabilizing olefin and in one case the reaction between the complex [Pd(η^2-dmfu)(DPPQ)] and dimethyl-maleate seems to indicate an exchange equilibrium constant of ca. 1×10^{-4} [11].

As for point (f) it is evident that the steric hindrance of the entering alkyne plays an important role in destabilizing the corresponding palladium(0) derivative. As a matter of fact, the equilibrium constant related to the bulky dbua is two orders of magnitude smaller than that of dma and deta although these are almost equivalent from the electronic point of view.

Points (g), and (e) summarize the efficiency of the substituent groups in the alkenes or alkynes in stabilizing the palladium(0) derivatives according to the following order:

$SO_2 > CN > COOCH_3 > C_6H_4NO_2$-4.

2.5. Comparison among equilibrium constants in complexes bearing different ancillary ligands

On the basis of the present and the already published data [6a,6b], we are able to propose Table 4 in which the K_E values were obtained when the same olefins are exchanged in substrates bearing different ancillary ligands. Whatever the ligand considered, the general olefin stabilization order is confirmed and the K_E values are almost always maintained within a narrow interval. The most surprising result is represented by the unusually high values of K_E when fn and ma are involved as entering olefins in complexes bearing ligands with *ortho*-substituted hetero-aromatic ring. It is evident (see bold numbers in Table 4) that the ratios between K_E for reactions involving the displacement of nq by fn or ma in complexes with an unsubstituted pyridine ancillary ring are usually considerably less than twenty (9.5 average). In the case of complexes with ligands bearing a substituted pyridine (or quinoline) ring the ratio jumps to 40 or more (cases concerning DPPQ-Me and MeN-SPh, respectively). Moreover, when Neocup is involved a marked increase is noticed and the values soar to 311 and 630, respectively (items 8, 9 of Table 3).

On the other hand, the ratios become directly comparable when the exchange between nq and dmfu is taken into account for any complex bearing different ancillary ligands (see column 2 in Table 4). Apparently, the efficiency in stabilizing the palladium(0) olefin complexes is markedly enhanced when olefins with reduced steric requirements and remarkable electron withdrawing capability are used. We surmise that the increase of the K_E values when fn and ma react with [Pd(η^2-nq)(Neocup)] and [Pd(η^2-dmfu)(Neocup)] is probably due to the steric release involved in the conversion of the crowded nq or dmfu complexes into the less hindered ma or fn derivative, but it is also caused by the increasing electronic density of palladium induced by the more basic substituted phenanthroline. This excess of charge is more efficiently delocalized by the electron poorer fn and ma olefins.

2.6. Kinetic measurements

We have also undertaken some kinetic studies taking advantage of the bulkiness of the olefin tetramethyl-ethylene-tetracarboxylate (tmetc) which, when coupled with the steric hindrance of the palladium(0) olefin derivatives, could induce a remarkable decrease in the olefin exchange reaction rates which otherwise are very fast. We have therefore studied the following reaction by means of ^{1}H NMR technique:

$$[Pd(\eta^2\text{-dmfu})(\text{L-L}')] + \text{tmetc} \rightarrow [Pd(\eta^2\text{-tmetc})(\text{L-L}')] + \text{dmfuL-L}' \quad (2)$$
$$= \text{DPPQ-Me, Neocup, Phen.}$$

The ensuing rate constants are markedly influenced by the nature of the ancillary ligand. Thus, the less hindered phenanthroline substrate reacts instantaneously, while the second order rate constant of its obvious counterpart [Pd(η^2-dmfu)(Neocup)] is about 3×10^{-4} mol^{-1} dm^3 s^{-1} [12]. Interestingly, the steric requirement of the Neocup moiety does not only influence the thermodynamic parameters (cfr. Table 4), but also the kinetics of the reaction, thereby confirming the associative nature of the olefin exchange. Stahl and co-workers pointed out that the rate of reactions involving olefins exchange would be increased by the nucleophilicity of palladium(0) center [13]. In this case, however, the enhanced nucleophilicity induced by Neocup on the metallic center appears to be overshadowed by the steric demand involved in the transition state.

On the other hand, the reactivity of the complex [Pd(η^2-dmfu)(DPPQ-Me)] can be determined by means of a second order kinetic study carried out under NMR conditions (Fig. 3) The corresponding rate constant ($k_2 = 0.31 \pm 0.01$ mol^{-1} dm^3 s^{-1}) lies between those of the less (Phen) and the more (Neocup) hindered derivatives and represents one of the few values determined for olefin exchange in palladium(0) complexes [6,13].

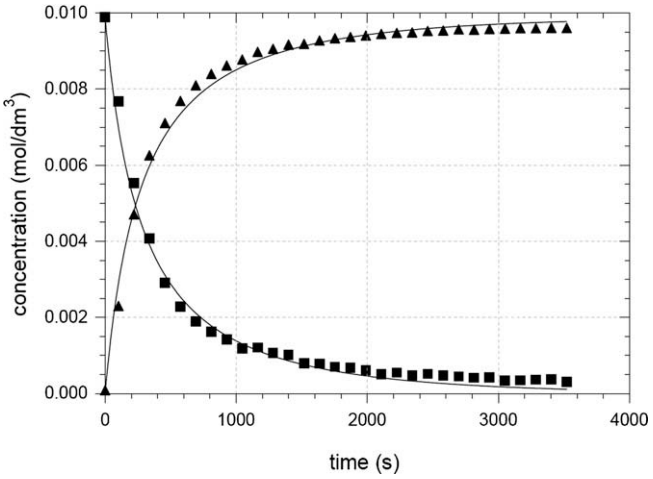


Fig. 3. Concentration profiles versus time determined by ^{1}H NMR technique at 25 °C in $CDCl_3$ for the reaction: [Pd(η^2-dmfu)(DPPQ-Me)] + tmetc[Pd(η^2-tmetc)(DPPQ-Me)] + dmfu[[Pd(η^2-dmfu)(DPPQ-Me)]]$_0$ = 9.9×10^{-3} mol dm^{-3}[tmetc]$_0$ = 1.26×10^{-2}.

[Pd(η^2-dmfu)(DPPQ-Me)] ■

[Pd(η^2-tmetc)(DPPQ-Me)] ▲

3. Conclusions

- We were able to prepare several complexes of palladium(0) bearing different ancillary ligands and alkenes or alkynes as stabilizing unsaturated molecules and to determine the structure of the complexes [Pd(η^2-dmfu)(DPPQ)] and [Pd(η^2-deta)(Neocup)]. The structure of the latter represents the first example of an alkyne derivative of palladium(0) with a N_2C_2 donor set.
- The exchange equilibrium constants between some complexes and the entering alkene or alkyne were determined by direct

Table 4
Comparative olefin exchange equilibrium constants for the reaction.

ol$_2$ / L-L′	dmfu	nq	fn	ma	K_{Ema}/K_{Efn}
[6b] HN-SMe		1	17	18	1.05
[6b] HN-SEt		1	12	16	1.33
[6b] HN-*Si*-Pr		1	6.7	9	1.35
[6b] HN-*St*-Bu		1	5.5	6.9	1.25
[6b] HN-SPh		1	8.4	7.2	0.86
[6b] MeN-SPh		1	**16**	**49**	3.06
BiPy	1.8×10^{-4}	1	2.5	4.8	1.92
Phen	*	1	3.9	10.7	2.74
DPPQ	3.0×10^{-4}	1	1.4	4.5	3.2
DPPQ-Me	3.8×10^{-4}	1	**12.1**	**38**	3.14
[6a] PyN_2	1×10^{-3}	1	4.55	8.17	1.80
Neocup	3.2×10^{-4}	1	**311**	**630**	2.02

[Pd(η^2-nq)(L-L′)] + ol$_2$ ⇌ [Pd(η^2-ol^2)(L − L′)] + nq.
Cases discussed in bold.
* Not determined for solubility problems.

spectrophotometric titration and a novel order comparing the different stabilizing character of both alkene and alkyne moieties was established for the first time.
- The coordinating capability order for the olefins was confirmed and the new entry *trans*-sulfone proved to be a quite strong coordinating moiety. Moreover, the *trans* olefins show an enhanced coordinating capability when compared with their *cis* counterparts. In the presence of similar electronic characteristics the stabilizing properties of the alkynes are strongly influenced by their steric demand.
- The nature of the ancillary ligands does not have a remarkable importance in stabilizing their palladium(0) derivatives. Only the presence of methyl groups in *ortho* position on the pyridine ring seems to enhance the stability of the complexes bearing fn and ma olefins. In this respect the neocuproine ligand proves to be the most effective.
- A kinetic determination of the reaction rates when the bulky tmetc was employed as entering alkene on the complex [Pd(η^2-dmfu)(DPPQ-Me)] was carried out by standard ^{1}H NMR technique.

4. Experimental

4.1. Solvents and reagents

Acetone and CH_2Cl_2 were distilled over CaH_2 and 4 Å molecular sieves, respectively. $CHCl_3$ was distilled over silver foil under inert atmosphere. All the other chemicals were commercially available grade products and were used as purchased. Unless otherwise stated, all manipulations were carried out under an argon atmosphere using standard Schlenk techniques.

The synthesis of the ligands 8-diphenylphosphanylquinoline (DPPQ) [14] and 8-diphenylphosphanyl-2-methylquinoline (DPPQ-Me) [15], the alkenes *cis*- and *trans*-1,2-bis[(4-methylphenyl)sulphonyl]ethene [16] (*cis*-sulf, *trans*-sulf) and the complexes [Pd(η^2-dmfu)(DPPQ-Me)], [Pd(η^2-dmfu)(DPPQ)] [11], [Pd(η^2-ma)(DPPQ-Me)] [4p], [Pd(η^2-dmfu)(Neocup)] [4t], [Pd(η^2-dmfu)(Phen)] [17] and [Pd(η^2-dmfu)(BiPy)] [18] was carried out according to published procedures.

4.2. Data analysis

Mathematical and statistical analysis of equilibrium and kinetic data was carried out by locally adapted non linear regression algorithms written under SCIENTIST™ environment.

4.3. IR, NMR, and UV-Vis measurements

The IR, ^{1}H and ^{13}C NMR spectra were recorded on a Perkin-Elmer Spectrum One spectrophotometer. 1D- and 2D-NMR spectra were recorded using a Bruker DPX300 or Bruker DPX500 spectrometer. Chemical shifts (ppm) are given relative to TMS (^{1}H and ^{13}C NMR) and 85% H_3PO_4 (^{31}P NMR). Peaks are labelled as singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m) and broad (br). The proton and carbon assignment was performed by ^{1}H-2D COSY, ^{1}H-2D NOESY, ^{1}H-^{13}C HMQC and HMBC experiments.

UV–Vis spectra were taken on a Perkin–Elmer Lambda 40 spectrophotometer equipped with a Perkin–Elmer PTP6 (Peltier temperature programmer) apparatus.

4.4. Preliminary studies and equilibrium measurements

All the equilibrium reactions were preliminarily studied by ^{1}H NMR technique by dissolving the complex under study in 0.6 ml of $CDCl_3$ ($[[Pd(\eta^2\text{-}ol_1)(L\text{-}L')]]_0$ $1 \div 3 \cdot 10^{-2}$ mol dm^{-3}) and adding microaliquots of a concentrated $CDCl_3$ solution of the exchanging olefin ol_2 according to reaction (1). The reaction progress was followed by monitoring the signal for the disappearance of the starting complex and the contemporary appearance of the final product [Pd(η^2-ol_2)(L-L′)]. The UV–Vis preliminary study was carried out by placing 3 ml of freshly prepared solution of the complex [Pd(η^2-ol_1)(L-L′)] ($[[Pd(\eta^2\text{-}ol_1)(L\text{-}L')]]_0 = 1 \cdot 10^{-4}$ mol dm^{-3}) in the thermostatted (298 K) cell compartment of the UV–Vis spectrophotometer. Microaliquots of solution containing the exchanging olefin ol_2 at adequate concentrations were added and the absorbance changes were monitored in the 250–400 nm wavelength interval or at fixed wavelength (320 nm); (in some cases where K_E was large an excess of free ol_1 had to be added to balance the equilibrium position).

4.5. X-ray analyses

Crystals suitable for X-ray work were obtained by slow diffusion of hexane in a dichloromethane solution for [Pd(η^2-dmfu)(DPPQ)] and of diethyl ether in a dichloromethane solution for [Pd(η^2-deta) (Neocup)]. The selected specimen of the [Pd(η^2-dmfu)(DPPQ)] complex was then fastened on the top of a glass fiber and transferred to a Nonius MACH3 diffractometer made available by Colleagues at the Department of Environmental Sciences of SUN, Caserta, Italy. The chosen item of [Pd(η^2-deta)(Neocup)] was inserted in a glass capillary and mounted on the goniometer head of a Philips PW1100 diffractometer at the C.N.R.-I.C.I.S. Institute of Padua, Italy. The raw data were collected at room temperature by using graphite-monochromated Mo Kα radiation (λ = 0.70930 Å on the MACH3 and λ = 0.71073 Å on the PW1100). Crystal stability was assessed by monitoring either a single ([Pd(η^2-dmfu)(DPPQ)]) or three ([Pd(η^2-deta)(Neocup)]) standard reflections every 200 measurements; neither of the two crystals showed sign of deterioration. Both structures were solved by direct methods and refined by standard full–matrix least–squares based on F_o^2 with the SHELXTL NT [19] and SHELXL-97 [20] programs. All non-hydrogen atoms were refined anisotropically; hydrogen atoms were included in idealized positions and refined as "riding model".

4.6. Crystal data for [Pd(η^2-dmfu)(DPPQ)]

$C_{27}H_{24}NO_4PPd$, fw = 563.8, monoclinic, space group $P2_1/c$ (No. 14), a = 17.380(4) Å, b = 9.421(2) Å, c = 16.273(3) Å, β = 111.38(3)°, V = 2481(1) Å^3, Z = 4, ρ = 1.509 g/cm^3, μ = 0.85 mm^{-1}. A total of 3533 unique reflections with $I > 2\sigma(I)$ were observed. Final agreement factors: R = 0.032, Rw = 0.078, GOF = 1.032.

4.7. Crystal data for [Pd(η^2-deta)(Neocup)]

$C_{22}H_{22}N_2O_4Pd$, fw = 484.8, monoclinic, space group $P2_1/n$ (No. 14), a = 16.280(3) Å, b = 7.889(1) Å, c = 16.988(3) Å, β = 109.16(3)°, V = 2061(1) Å^3, Z = 4, ρ = 1.562 g/cm^3, μ = 0.93 mm^{-1}. A total of 4576 unique reflections with $I > 2\sigma(I)$ were observed. Final agreement factors: R = 0.043, Rw = 0.104, GOF = 1.201. Additional crystallographic data (atomic coordinates, full listings of bond lengths and angles, anisotropic thermal parameters) are available as Supporting information (pdq.cif for [Pd(η^2-dmfu)(DPPQ)], can.cif for [Pd(η^2-deta)(Neocup)]).

4.8. Synthesis of [Pd(η^2-nq)(DPPQ)]

To a solution of nq (0.0389 g, 0.246 mmol) and DPPQ (0.0763 g, 0.244 mmol) in dry acetone (15 ml) solid $Pd_2DBA_3 \cdot CHCl_3$ [21] (0.120 g, 0.116 mmol) was added under inert atmosphere (Argon). The reaction mixture was stirred for 1 h

at room temperature and the initial dark suspension turned to an orange solution which was taken to dryness under reduced pressure and the residue re-dissolved in dichloromethane. Addition of charcoal and filtration on celite removed the traces of metallic palladium yielding a clear orange solution. Reduction to small volume (3–4 cm^3) and slow addition of diethyl ether gave the product as microcrystalline orange solid (0.1014 g, yield ~76%).

Selected data: ^1H NMR (300 MHz, $CDCl_3$, T = 298 K, ppm) δ: 5.03 (dd, 1H, J_{PH} = 9.2 Hz, CH=CH $J_{CH=CH}$ = 6.9 Hz, *trans*-P); 5.22 (d, 1H, $J_{CH=CH}$ = 6.9 Hz, CH=CH *trans*-N); 7.18–7.70 (m, 12H, H^c, PPh_2), 7.66 (t; H, J = 8.2 Hz; H^6); 7.68 (dd; H, J = 8.3 Hz; J = 4.7 Hz; H^3); 7.90–8.07 (m, 4H, H^7, H^5, H^b); 8.36 (d; 1H, J = 8.3 Hz; H^4); 9.07 (d; 1H, J = 4.7 Hz; H^2). $^{31}P\{^1H\}$ NMR ($CDCl_3$, T = 298 K, ppm) δ: 25.3 $^{13}C\{^1H\}$ NMR ($CDCl_3$, T = 298 K, ppm) δ: 64.6 (CH, CH=CH *trans*-N); 70.3 (d, CH, J_{CP} = 17.6 Hz CH=CH *trans*-P); 123.5 (CH, C^3); 124.6, 125.2 (CH, C^b); 127.5 (d, CH, J_{CP} = 4.8 Hz, C^6); 131.0 (CH,C^5); 130.5, 131.4 (CH, C^c); 134.6 (d,C, J_{CP} = 35.0 Hz, C^8); 136.5, (C, C^a *trans*-N); 137.0 (C, C^a *trans*-P); 137.7 (d, CH, J_{CP} = 2.3 Hz, C^7); 138.4 (CH, C^4); 150.0 (C, C^9); 151.3 (C, C^{10}); 152.2 (CH, C^2); 177.1 (d, CO, J_{CP} = 6.3 Hz CO *trans*-N); 183.4 (CO, CO *trans*-P). IR(KBr pellet) ν = 1636, 1622, 1588 cm^{-1} (C=O). Anal. Calc. for $C_{31}H_{22}NO_2PPd$: C, 64.43; H, 3.84; N, 2.42. Found: C, 64.27; H, 3.94; N, 2.50%.

The following complexes were synthesized in an analogous way using $Pd_2DBA_3 \cdot CHCl_3$, the appropriate ligand and alkene or alkyne, in the same molar ratios.

4.9. [Pd(η^2-nq)(DPPQ-Me)]

Yield: ~80% (orange solid). Selected data: ^1H NMR (300 MHz, $CDCl_3$, T = 298 K, ppm)) δ: 3.14 (s, 3H, quinoline-CH_3) 5.01 (m, 2H, CH=CH *trans*-P and *trans*-N); 7.06–7.13 (m, 2H, PPh_2), 7.29–7.35 (m, 2H, PPh_2), 7.38–7.47 (m, 6H, H^c, PPh_2), 7.48–7.62 (m, 4H, H^3, H^6 PPh_2); 7.69 (d; H, J = 7.3 Hz; H^b); 7.86 (t, 1H, J = 7.5 Hz H^7); 7.90 (d; H, J = 7.9 Hz; H^5); 8.04 (d; H, J = 7.3 Hz; H^b); 8.19 (d; 1H, J = 8.4 Hz; H^4). $^{31}P\{^1H\}$ NMR ($CDCl_3$, T = 298 K, ppm) δ: 25.4. $^{13}C\{^1H\}$ NMR ($CDCl_3$, T = 298 K, ppm) δ: 30.2 (CH_3, quinoline–CH_3); 62.6 (CH, CH=CH *trans*-N); 66.2 (d, CH, J_{CP} = 21.0 Hz CH=CH *trans*-P); 123.8 (CH, C^3); 125.0, 125.4 (CH, C^b); 126.3 (d, CH, J_{CP} = 4.8 Hz, C^6); 131.0 (CH,C^5); 130.1, 131.2 (CH, C^c); 134.3 (d,C, J_{CP} = 35.1 Hz, C^8); 136.0, (C, C^a *trans*-N); 136.5 (C, C^a *trans*-P); 137.8 (d, CH, J_{CP} = 2.3 Hz, C^7); 138.3 (CH, C^4); 151.2 (C, C^9); 151.5 (C, C^{10}); 165.6 (C, C^2); 184.0 (d, CO, J_{CP} = 5.6 Hz CO *trans*-N); 185.1 (CO, CO *trans*-P). IR(KBr pellet) ν = 1637, 1622, 1587 cm^{-1} (C=O). Anal. Calc. for $C_{32}H_{24}NO_2PPd$: C, 64.93; H, 4.09; N, 2.37. Found: C, 64.64; H, 4.14; N, 2.27%.

4.10. [Pd(η^2-ma)(DPPQ)]

Yield: ~80% (yellow solid). Selected data: ^1H NMR (300 MHz, $CDCl_3$, T = 298 K, ppm)) δ: 4.11 (dd, 1H, J_{PH} = 10.3 Hz, CH=CH $J_{CH=CH}$ = 3.7 Hz, *trans*-P); 5.22 (dd, 1H, $J_{CH=CH}$ = 3.7 Hz, J_{PH} = 3.1 Hz, CH=CH *trans*-N); 7.35–7.61 (m, 11H, H^3, PPh_2), 7.71 (t; H, J = 7.8 Hz; H^6); 7.95 (t; H, J = 7.8 Hz; H^7); 8.02 (d; H, J = 7.8 Hz; H^5); 8.41 (d; 1H, J = 8.3 Hz; H^4); 9.40 (d; 1H, J = 4.7 Hz; H^2). $^{31}P\{^1H\}$ NMR ($CDCl_3$, T = 298 K, ppm) δ: 23.3. $^{13}C\{^1H\}$ NMR ($CDCl_3$, T = 298 K, ppm) δ: 48.0 (CH, CH=CH *trans*-N); 48.4 (d, CH, J_{CP} = 31.0.6 Hz CH=CH *trans*-P); 123.1 (CH, C^3); 127.8 (d, CH, J_{CP} = 5.0 Hz, C^6); 130.5 (d, C, J_{CP} = 37.5 Hz, C^8); 131.2 (CH, C^5); 138.0 (d, CH, J_{CP} = 2.1 Hz, C^7); 138.6 (CH, C^4); 150.7 (C, C^9); 151.0 (C, C^{10}); 156.4 (CH, C^2); 171.7 (d, CO, J_{CP} = 5.3 Hz CO *trans*-N); 172.7 (CO, CO *trans*-P). IR(KBr pellet) ν = 1793, 1713 cm^{-1} (C=O). Anal. Calc. for $C_{25}H_{18}NO_3PPd$: C, 57.99; H, 3.50; N, 2.70. Found: C, 57.70; H, 3.64; N, 2.78%.

4.11. [Pd(η^2-deta)(Neocup)]

Yield: ~65% (yellow solid). Selected data: ^1H NMR (300 MHz, $CDCl_3$, T = 298 K, ppm) δ: 1.37 (t, 6H, J = 7.1 Hz, ethyl-CH_3); 3.12 (s, 6H, neocuproine-CH_3); 4.33 (q, 4H, J = 7.1 Hz, ethyl-CH_2); 7.69 (d, 2H, J = 8.3 Hz, H^3); 7.76 (s, 2H, H^5); 8.24 (d, 2H, J = 8.3 Hz, H^4). $^{13}C\{^1H\}$ NMR ($CDCl_3$, T = 298 K, ppm) δ: 14.4 (CH_3, ethyl-CH_3); 29.9 (CH_3, neocuproine-CH_3); 60.6 (CH_3, ethyl-CH_2); 110.0 (C, C≡C); 124.9 (CH, C^3); 125.5 (CH, C^5); 127.2 (C, C^6); 136.6 (CH, C^4); 145.4 (C, C^7); 161.4 (C, C^2); 163.7 (CO, CO). IR(KBr pellet) ν = 1842, 1675 cm^{-1} (C=O). Anal. Calc. for $C_{22}H_{22}N_2O_4Pd$: C, 54.50; H, 4.57; N, 5.78. Found: C, 54.65; H, 4.64; N, 5.82%.

4.12. [Pd(η^2-dbua)(Neocup)]

Yield: ~70% (yellow solid). Selected data: ^1H NMR (300 MHz, $CDCl_3$, T = 298 K, ppm) δ: 1.59 (s, 18H, *t*-Bu); 3.17 (s, 6H, neocuproine-CH_3); 7.68 (d, 2H, J = 8.3 Hz, H^3); 7.75 (s, 2H, H^5); 8.23 (d, 2H, J = 8.3 Hz, H^4). $^{13}C\{^1H\}$ NMR ($CDCl_3$, T = 298 K, ppm) δ: 28.4 (CH_3, *t*-Bu); 30.2 (CH_3, neocuproine-CH_3); 80.3 (C, *t*-Bu); 110.6 (C, C≡C); 124.7 (CH, C^3); 125.4 (CH, C^5); 127.2 (C, C^6); 136.5 (CH, C^4); 145.4 (C, C^7); 161.3(C, C^2); 162.8 (CO, CO). IR(KBr pellet) ν = 1803, 1680 cm^{-1} (C=O). Anal. Calc. for $C_{26}H_{30}N_2O_4Pd$: C, 57.73; H, 5.59; N, 5.18. Found: C, 57.64; H, 4.66; N, 5.25%.

4.13. [Pd(η^2-trans-sulf)(Neocup)]

Yield: ~80% (pale yellow solid). Selected data: ^1H NMR (300 MHz, $CDCl_3$, T = 298 K, ppm) δ: 2.39 (s, 6H, tol-CH_3); 3.40 (s, 6H, neocuproine-CH_3); 4.17 (s, 2H, CH=CH); 6.96 (d, 4H, J = 8.0 Hz, H^c); 7.42 (d, 4H, J = 8.0 Hz, H^b); 7.71 (d, 2H, J = 8.3 Hz, H^3); 7.78 (s, 2H, H^5); 8.27 (d, 2H, J = 8.3 Hz, H^4). $^{13}C\{^1H\}$ NMR ($CDCl_3$, T = 298 K, ppm) δ: 21.5 (Ph-CH_3); 30.8 (CH_3, neocuproine-CH_3); 54.3 (CH, C=C); 125.45 (CH, C^3); 125.47 (CH, C^5); 126.4 (CH, C^b); 127.3 (C, C^6); 129.1 (CH, C^c); 137.4 (CH,C^4); 139.5 (C, C^a); 141.7 (C, C^d); 146.0 (C, C^7); 162.4 (C, C^2); IR(KBr pellet) ν = 1287, 1140 cm^{-1} (S=O). Anal. Calc. for: $C_{28}H_{27}NO_4PdS_3$: C, 52.21; H, 4.22; N, 2.17. Found: C, 52.14; H, 4.28; N, 2.26%.

4.14. [Pd(η^2-nq)(Neocup)]

0.0130 g (0.082 mmol) of naphthoquinone was added to a solution of 0.0360 g (0.079 mmol) of [Pd(η^2-dmfu)(Neocup)] in 5 ml of anhydrous CH_2Cl_2. Immediate precipitation of an orange solid was observed and the reaction mixture was stirred for 30 min. The solution was concentrated under reduced pressure and the precipitation was completed by addition of diethyl ether. The orange product was filtered off (G4) and washed with small aliquots of diethyl ether and pentane and dried under vacuum. Yield 0.0360 g, ~96%. Selected data: ^1H NMR (300 MHz, $CDCl_3$, T = 298 K, ppm) δ: 3.09 (s, 6H, neocuproine-CH_3); 4.86 (s, 2H, CH=CH); 7.41 (m, 2H, H^c); 7.66 (d, 2H, J = 8.3 Hz, H^3); 7.72 (s, 2H, H^5); 7.97 (m, 2H, H^b); 8.21 (d, 2H, J = 8.3 Hz, H^4). $^{13}C\{^1H\}$ NMR ($CDCl_3$, T = 298 K, ppm) δ: 30.0 (CH_3, neocuproine-CH_3); 55.3 (CH, CH=CH); 125.2 (CH, C^b); 125.4 (CH, C^3); 125.6 (CH, C^5); 127.4 (C, C^6); 131.2 (CH, C^c); 137.1 (CH, C^4); 145.6 (C, C^7); 163.0 (C, C^2); 188.2 (CO, naphthoquinone-CO). IR(KBr pellet) ν = 1627, 1588 cm^{-1} (C=O). Anal. Calc. for $C_{24}H_{18}N_2O_2Pd$: C, 60.96; H, 3.84; N, 5.92. Found: C, 60.78; H, 3.78; N, 5.82%.

4.15. [Pd(η^2-ma)(Neocup)]

This complex was synthesized in an analogous way using ma as entering alkene. Yield: ~83% (pale yellow solid). Selected data: ^1H NMR (300 MHz, $CDCl_3$, T = 298 K, ppm) δ: 3.16 (s, 6H, neocuproine-CH_3); 4.15 (s, 2H, CH=CH); 7.74 (d, 2H, J = 8.3 Hz, H^3); 7.82 (s, 2H,

H^5); 8.27 (d, 2H, J = 8.3 Hz, H^4). IR(KBr pellet) ν = 1787, 1722 cm^{-1} (C=O). Anal. Calc. for $C_{18}H_{14}N_2O_3Pd$: C, 52.38; H, 3.42; N, 6.79. Found: C, 52.27; H, 3.36; N, 6.94%.

4.16. [Pd(η^2-nq)(Phen)]

0.0154. g (0.098 mmol) of naphthoquinone was added to a solution of 0.0400 g (0.093 mmol) of [Pd(η^2-dmfu)(Phen)] in 5 ml of anhydrous CH_2Cl_2. Immediate precipitation of an orange solid was observed and the reaction mixture was stirred for 30 min. The solution was concentrated under reduced pressure and the precipitation was completed by addition of diethyl ether. The orange product was filtered off (G4) and washed with small aliquots of diethyl ether and pentane and dried under vacuum. Yield 0.0385 g, ~93%. Selected data: ^{1}H NMR (300 MHz, $CDCl_3$, T = 298 K, ppm) δ: 5.03 (s, 2H, CH=CH); 7.44 (m, 2H, H^c); 7.81 (dd, 2H, J = 8.3 Hz, J = 4.8 Hz, H^3); 7.83 (s, 2H, H^5); 8.08 (m, 2H, H^b); 8.38 (dd, 2H, J = 8.2 Hz, J = 1.5 Hz, H^4) 8.95 (dd, 2H, J = 4.3 Hz, J = 1.5 Hz, H^2). $^{13}C\{^1H\}$ NMR ($CDCl_3$, T = 298 K, ppm) δ: 125.0 (CH, C^b); 125.4 (CH, C^3); 126.7 (CH, C^5); 129.2 (C, C^6); 130.9 (CH, C^c); 137.0 (C, C^a) 137.2 (CH, C^4); 145.1 (C, C^7); 150.4 (C, C^2); 179.3 (CO, naphthoquinone-CO). CH, CH=CH not detectable. IR (KBr pellet) ν = 1616, 1583 cm^{-1} (C=O). Anal. Calc. for $C_{22}H_{14}N_2O_2Pd$: C, 59.41; H, 3.17; N, 6.30. Found: C, 59.50; H, 3.23; N, 6.89%.

4.17. [Pd(η^2-ma)(Phen)]

This complex was synthesized in an analogous way using ma as entering alkene. Yield: ~88% (yellow solid). Selected data: ^{1}H NMR (300 MHz, $CDCl_3$, T = 298 K, ppm) δ: 4.17 (s, 2H, CH=CH); 7.84 (dd, 2H, J = 8.2 Hz, J = 4.8 Hz, H^3); 7.96 (s, 2H, H^5); 8.49 (dd, 2H, J = 8.2 Hz, J = 1.5 Hz, H^4) 9.25 (dd, 2H, J = 4.8 Hz, J = 1.5 Hz, H^2). IR(KBr pellet) ν = 1796, 1720 cm^{-1} (C=O). Anal. Calc. for $C_{16}H_{10}N_2O_3Pd$: C, 49.96; H, 2.62; N, 7.28. Found: C, 49.80; H, 2.70; N, 7.36%.

4.18. [Pd(η^2-nq)(BiPy)]

0.0163 g (0.103 mmol) of naphthoquinone was added to a solution of 0.0400 g (0.079 mmol) of [Pd(η^2-dmfu)(BiPy)] in 5 ml of anhydrous CH_2Cl_2. Immediate precipitation of an orange solid was observed and the reaction mixture was stirred for 30 min. The solution was concentrated under reduced pressure and the precipitation was completed by addition of diethyl ether. The orange product was filtered off (G4) and washed with small aliquots of diethyl ether and pentane and dried under vacuum. Yield 0.0408 g, ~94%. Selected data: ^{1}H NMR (300 MHz, $CDCl_3$, T = 298 K, ppm) δ: 4.92 (bs, 2H, CH=CH); 7.45 (m, 2H, H^c); 7.50 (ddd, 2H, J = 7.5 Hz, J = 5.1 Hz, J = 1.9 Hz, H^3); 7.94 (m, 4H, H^5, H^4); 8.08 (m, 2H, H^b); 8.65 (d, 2H, J = 5.1 Hz, H^2). IR (KBr pellet) ν = 1616, 1582, 1565 cm^{-1} (C=O). Anal. Calc. for $C_{20}H_{14}N_2O_2Pd$: C, 57.06; H, 3.35; N, 6.66. Found: C, 57.14; H, 3.28; N, 6.78%.

4.19. [Pd(η^2-ma)(BiPy)]

This complex was synthesized in an analogous way using ma as entering alkene. Yield: ~93% (pale yellow solid). Selected data: ^{1}H NMR (300 MHz, $CDCl_3$, T = 298 K, ppm) δ: 4.04 (s, 2H, CH=CH)); 7.53 (ddd, 2H, J = 7.5 Hz, J = 5.0 Hz, J = 1.9 Hz, H^3); 8.05 (m, 4H, H^5, H^4); 8.94 (d, 2H, J = 5.0 Hz, H^2). IR(KBr pellet) ν = 1783, 1720 cm^{-1} (C=O). Anal. Calc. for $C_{14}H_{10}N_2O_3Pd$: C, 46.62; H, 2.79; N, 7.77. Found: C, 46.80; H, 2.70; N, 7.66%.

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Appendix A. Supplementary material

Figure concerning the equilibrium titration curves for the determination of equilibrium exchange constants and X-ray crystallographic data. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2008.11.012.

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