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Cationic Platinum(II)- or Palladium(II)-carbyl complexes and unsaturated substrates: a facile way to C–C bond formation

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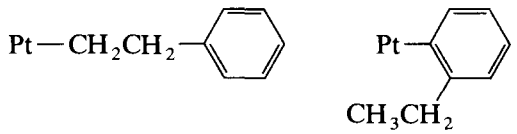
Abstract

Alkenes, alkynes, 1,2- and 1,3-dienes react with $[MR(N-N)(MeCN)]^+$ (M = Pt or Pd; R = hydrocarbyl group; N–N = bidentate nitrogen ligand) to give R-substituted derivatives. The organic fragment is generally retained within the metal environment in η^1 or η^3 coordination, except in the reaction of alkenes with $Pd^{(II)}$ complexes. In this case, a free R-substituted alkene is produced via a relatively fast β-elimination process from a Pd-alkyl intermediate. Different regiochemistries are detected in the reaction between monosubstituted olefins (propene or styrene) and homologous Pt and Pd complexes. The Pt–C bond is always formed with the terminal unsubstituted alkene carbon, while a preference toward the internal carbon, particularly if phenyl-substituted, is observed with Pd species. Neutral [MClR(N–N)] are markedly less reactive. In this case, when M = Pt, the unsaturated organic substrate generally adds to the metal affording fairly stable *tbp* five-coordinate complexes.

Keywords: Platinum; Palladium; Synthesis; C–C bond formation

1. Introduction

A novel C–C bond formation arising from the reaction between ethylene (or a higher alkene) and a metal σ-bound aryl in a PtII cationic complex has been recently [1] reported. Two different products are obtained, i.e. a 2-aryl-ethylplatinum(II) or a 2-ethylaryl platinum(II) complex, according to whether ethylene is



added to a four-coordinate $[PtR(N,N\text{-chelate})(MeCN)]^+$ (R = aryl) compound, or the olefin is already present in the metal coordination sphere of a previously synthesized five-coordinate *tbp* species $[PtR(C_2H_4)(N,N\text{-chelate})(MeCN)]^+$. When R = Me, we failed to obtain comparable results under the same experimental conditions. Methyl migration onto the unsaturated ligand was instead observed when alkynes were tested as substrates [2].

To obtain further information on the above process, the behaviour of dienes with cumulated and conjugated double bonds was examined. Because it is known [3] that the Pd–R bond is prone to add to a variety of unsaturated substrates, five- and four-coordinate neutral and cationic species [PdMeX(N,N-chelate)(uns)] and [PdRX(N,N-chelate)] (X = Cl or MeCN; uns = unsaturated ligand) have been used. In this paper we report the results obtained and make a comparison between the behaviour of PtII and PdII complexes.

2. Results and discussion

2.1. Platinum complexes with dienes

Cumulated dienes such as 1,2-propadiene and its homologues are reported to form square-planar PtII complexes [4] displaying chemical properties fairly similar to those of mono-ene derivatives. In contrast, very

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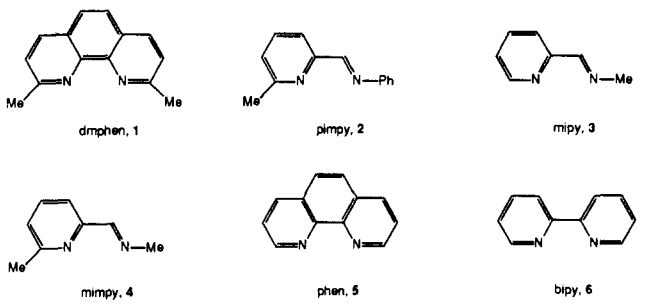
few [5] examples of five-coordinate PtII *tbp* adducts with cumulated dienes are known.

When 1,1-dimethylallene (DMA) was added to suitable four-coordinate compounds of the type [PtClR(N–N)] (R = hydrocarbyl group; N–N = bidentate nitrogen ligand, Scheme 1), white crystalline compounds could be isolated in good yields in the case of N–N = **1** or **2**

$$[PtClR(N\text{–}N)] + DMA = [PtClR(DMA)(N\text{–}N)] \quad (1)$$

When less crowded N–N were used (**3–6**), no DMA addition was observed at room temperature. The requirements of the nitrogen chelate in order to favour expansion of the metal coordination by taking up an unsaturated ligand, have been extensively reported elsewhere [6]. The five-coordinate adducts were characterized by the usual procedures and their ^{1}H and ^{13}C NMR data are listed in Table 1. The assignment of a *tbp* geometry with the DMA in equatorial position



Scheme 1.

Table 1
Relevant $^{1}H[^{13}C]$ NMR data for [PtClR(N–N)(diene)] complexes [a]

Entry	N–N,diene	R	Pt–R	Pt–π–[C]$_{olef}$H	Me–C(Het)	Others
I	**1** [b],DMA	Me	−0.07(74,s)	3.25(82,bs,1H), [c] (1H)	3.60(s), 3.39(s)	2.17(s,Me), 2.07(s,Me)
			[−10.8(634)]	[12.2(235,=CH_2), 131.3 (730,=C=)]	[31.0,27.5]	[110.7(CMe_2), 27.8(102,Me), 22.0(43,Me)]
II		Et [d]	0.8([e],2q,CH_2); −0.08(54,t,Me)	3.25(81,bs,1H), 2.02(61,bs,1H)	3.55(s), 3.31(s)	2.18(s,Me), 2.08(s,Me)
			[14.2(677,CH_2); 16.0(27,Me)]	[11.9(270,=CH_2), 129.8 ([e],=C=)]	[32.9,28.4]	[108.5(CMe_2), 28.9(110,Me), 21.2(44,Me)]
III		4-MeOPh	6.52(44,d,2H); 6.14(d,2H)	3.28(76,bs,1H), 2.45(64,bs,1H)	3.60(s), 3.47(s)	3.52(s,OMe); 2.15(s,Me), 2.09(s,Me)
			[156.0(C4),136.2 (C1), 133.3(C2,C6), 12.8(C3,C5)]	[15.4(224,=CH_2),[c] (=C=)]	[30.5,27.2]	[109.5(CMe_2); 54.7(OMe); 27.6([e],Me), 20.7(41,Me)]
IV	**1**,BD	Me [f]	0.02(71,s)	[c] (=CH); 3.25([e],d,C*H*H), 2.45(66,d,CH*H*)	3.34(s), 3.28(s)	6.57(dt,=CH), 5.42(d,C*H*H), 5.29(d,CH*H*)
			0.08(71,s)	4.35(91,m,=CH); 3.23([e], d,C*H*H), 2.52(52,d,CH*H*)	3.38(s), 3.35(s)	5.95(dt,=CH), 5.53(d,C*H*H), 5.33(d,CH*H*)
V		4-MeOPh [g]	6.68(40,d,2H); 6.58(40,d,2H); 6.20(d,2H); 6.12(d,2H)	4.45(95,m,=CH), [c] (=CH); [c] (2 C*H*H), 2.72(54,d,CH*H*), 2.70(61,d,CH*H*)	3.49(s), 3.48(s)	[c] (=CH), 4.98(m,=CH), 5.5(m,2 C*H*H), 5.36(d,CH*H*), 5.14(d, CH*H*); 3.61(OMe), 3.60(OMe)
VI	**2** [h],DMA	Me	0.04(72,s)	2.97(81,bs,1H) [c], (1H)	3.18(s)	8.88(37,s,CH=N); 1.94(s,Me), 1.27(s,Me)
			[−12.5(644)]	[11.3(254,=CH_2), 132.2 (627,=C=)]	[29.1]	[163.4(CH=N); 109.1(CMe_2), 25.3(93,Me), 20.5(42,Me)]
VII		Et	1.12(60,q,C*H*H), 0.85(68,q,CH*H*); 0.22(54,t,Me)	3.22(87,bs,1H), 2.00(67,bs,1H)	3.13(s)	8.82(37,s,CH=N); 1.93(s,Me), 1.33(s,Me)
			[12.8(610,CH_2); 15.5(34,Me)]	[11.5(248,=CH_2), 132.0 (626,=C=)]	[27.3]	[163.8(CH=N); 108.8(CMe_2), 25.6(102,Me), 20.7(41,Me)]
VIII		4-MeOPh	6.67(41,d,2H), 6.36(d,2H)	3.09(87,bs,1H), 2.25(68,bs,1H)	3.40(s)	8.70(37,s,CH=N); 3.64(s,OMe); 1.89(s,Me), 1.53(s,Me)
IX	**2**,BD	Me	0.01(72,s)	[c] (=CH), [c] (C*H*H), 2.36 (45,d,CH*H*)	3.11(s)	9.08(33,s,CH=N); 5.9(m,=CH), [c] (=CH_2)

[a] Spectra recorded in $CDCl_3$ or $C_2D_2Cl_4$ (reference δ 7.26, $CHCl_3$ [δ 77.0, $^{13}CDCl_3$] and δ 5.98, C_2HDCl_4 [δ 74.15, $^{13}C_2D_2Cl_4$]). The coupling constants with ^{195}Pt (Hz) are reported in parentheses. Abbreviations: s(singlet), bs(broad singlet), d(doublet), t(triplet), dt(double triplet), m(multiplet); in the multiplicity assignment, the geminal coupling (2 ÷ 4 Hz) has been ignored. [b] The chemical shifts of the N–N protons and carbons not listed in the table are approximately at δ: 8.4–8.3(two d,2H), 7.9(s,2H), 7.8–7.7(two, d,2H) [162(C2, C9), 145(2 quat C–N), 138(C4, C7), 129(2 C), 126(4 C)]. [c] Obscured by other signals. [d] As iodo derivative. [e] Coupling constant with ^{195}Pt not evaluable. [f] Two stereoisomers in ca. 7:3 ratio. [g] Two stereoisomers in ca. 1:1 ratio. [h] The chemical shifts of the N–N protons and carbons not listed in the table are approximately at δ: 7.9(t,1H), 7.8(two d,2H), 7.3–7.6(m,5Ar–H) [162(C6),151.5(C2), 150.5(34,=NC_{Ph}), 138.5(C4), 129(2Ar–C), 128–126(C5,C3,1Ar–C), 122.0(2Ar–C)].

stems from the comparison of their spectral data with those reported for the already known alkene- and alkyne-PtII five-coordinate complexes [2,6]. DMA coordinates to the metal through the less substituted double bond, as clearly shown by the NMR parameters. In particular, the high-field shift compared to the proligand for resonances of the carbon atoms involved in the metal–DMA bond [compare 132 vs. 206.6 δ (=C=) and 11–15 vs. 72.5 δ (=CH_2) with 110 vs. 93.9 δ (=CMe_2) are to be noted. In addition, hindered rotation of the unsaturated ligand around the Pt–DMA bond gives rise to a noticeable difference (1 ÷ 1.2 ppm) in the chemical shifts of the two =CH_2 protons, the signal at higher δ being attributable to the hydrogen facing the axial halogen [7]. With the N–N ligand **2**, which has chemically non-equivalent nitrogen atoms, only one rotational isomer was isolated in the solid state, and no isomerization was observed in solution. Unfavourable steric interactions of the CMe_2 group of DMA with the 6-Me-substituted pyridine ring of **2** could account for this.

All the complexes obtained except one, are stable in solution for days, and no DMA release or other decomposition processes is detected. However, five-coordinate [PtCl(4-MeOPh)(DMA)(pimpy)] slowly transforms into a π-allylic derivative through the aryl migration to the coordinated DMA double bond, the reaction being complete within one week at room temperature. A similar reaction was observed when attempts were made to obtain five-coordinate cationic DMA complexes by chlorine abstraction in presence of MeCN from the corresponding neutral species.

$$[PtClR(CH_2{=}C{=}CMe_2)(N{-}N)] + AgBF_4 + MeCN = [PtR(CH_2{=}C{=}CMe_2)(N{-}N)(MeCN)]BF_4 + AgCl \quad (2)$$

$$[PtR(CH_2{=}C{=}CMe_2)(N{-}N)(MeCN)]BF_4 = [Pt(CH_2{-}CR{-}CMe_2)(N{-}N)]BF_4 + MeCN \quad (3)$$

The migratory insertion process is very fast when R = aryl and the square-planar π-allylic derivative (Eq.

Table 2
Relevant ^1H NMR data for $[M(CH_2{-}CR{-}CMe_2)(N{-}N)]BF_4$ complexes [a]

Entry	M	N–N	R	CH_2	C–R	CMe_2	Me(H)–C(Het)	Others
X	Pt	1	Me	4.05(18,d,11-*syn*) 3.10([b],d,H-*anti*)	2.07(90,s)	1.50([b],s), 1.46([b],s)	3.27(s) 3.15(s)	
XI			4-MeOPh	3.98(12,d,H-*syn*) 3.53(68,d,H-*anti*)	7.72(d,2H), 6.69(d,2H)	1.59(20,s), 1.35(18,s)	3.18(bs), 3.10(bs)	3.67(s,OMe)
XII		2	Me	4.01(17,d,H-*syn*) 3.08(70,d,H-*anti*)	2.07(85,s)	1.11(15,s), 0.45(10,s)	2.93(s)	9.43(73,s,N=CH)
XIII			Et	4.00(17,d,H-*syn*) 3.04(72,d,H-*anti*)	2.4([b],m,CH_2), 1.10(t,Me)	1.12(17,s) 0.48(11,s)	2.95(s)	9.32(72,s,N=CH)
XIV			4-MeOPh	3.97(12,d,H-*syn*) 3.44(68,d,H-*anti*)	7.20(d,2H), 6.82(d,2H)	1.30(15,s), \0.32(10,s)	2.95(s)	9.43(71,s,N=CH), 3.80(s,OMe)
XV			4-MeOPh [e]	3.82([b],d,H-*syn*) 3.09(67,d,H-*anti*)	7.40(d,2H) 6.75(d,2H)	1.32(20,s) 0.72(15,s)	2.95(s)	10.04(44,s,N=CH), 3.80(s,OMe)
XVI			CH_2Ph	3.81(10,d,H-*syn*) 3.06(70,d,H-*anti*)	3.55([b],ABq)	1.12(17,s), 0.52(10,s)	2.60(s)	9.39(71,s,N=CH)
XVII		3	4-MeOPh [c]	3.75([b],d,H-*syn*) 3.73([b],d,H-*syn*) 3.56(70,d,H-*anti*) 3.42(70,d,H-*anti*)	7.26(m), 6.90(m)	1.58([b],s), 1.55([b],s), 1.45([b],s) 1.44([b],s)	9.04(30,d), 8.67(30,d)	9.59(82,s,N=CH), 9.49 (75,s,N=CH), 3.80(s,2 OMe), 4.21(35,s,NMe), 3.98(32,s,NMe)
XVIII		4	4-MePh	[d] (H-*syn*) 3.44(72,d,H-*anti*)	7.22(d,2H), 7.16(d,2H)	1.43([b],s), 1.41([b],s),	2.85(s)	9.58(78,s,N=CH), 3.95 (33,s,NMe), 2.35(s,Me)
XIX		5	COMe	4.31(17,d,H-*syn*) 3.50(67,d,H-*anti*)	2.50(s,Me)	1.80(10,s), 1.50(10,s)	9.58(34,d), 9.30(34,d)	
XX	Pd	1	Me	4.23(s,H-*syn*) 3.71(s,H-*anti*)	2.05(s)	1.60(s), 1.55(s)	3.11(s)	
XXI			Me [e]	3.75(s,H-*syn*) 3.09(s,H-*anti*)	2.17(s)	0.60(s), 0.45(s)	3.26(s)	
XXII			COMe [e]	4.36(bs,H-*syn*) 3.30(bs,H-*anti*)	2.69(s,Me)	0.69(s), 0.46(s)	3.17(s)	
XXIII		2	Me	4.18(s,H-*syn*) 3.54(s,H-*anti*)	2.03(s)	1.19(s) 0.60(s)	2.79(s)	8.75(s,N=CH)
XXIV			Me [e]	3.66(s,H-*syn*) 3.13(s,H-*anti*)	2.03(s)	1.36(s) 1.23(s)	2.73(bs)	8.75(bs,N=CH)
XXV		5	Me	[d] (H-*syn*) 3.95(s,H-*anti*)	2.05(s)	1.88(s), 1.50(s)	9.25(m), 9.10(m)	

[a] Spectra recorded in $CDCl_3/CD_3NO_2$ mixture (reference δ 7.26, $CHCl_3$). The coupling constants with ^{195}Pt (Hz) are reported in parentheses. Abbreviations: s(singlet), bs(broad singlet), d(doublet), t(triplet), q(quartet), m(multiplet). [b] Coupling constant with ^{195}Pt not evaluable. [c] Two geometrical isomers in 1:1 ratio. [d] Obscured by other signals. [e] As chloro derivative.

3) is the only identified reaction product. In the case of R = Me, a five-coordinate cationic species (Eq. 2) can be detected in solution and the π-allylic complex quantitatively forms on standing (24 h and 48 h in the case of N–N = **2** and **1**, respectively). The presence of a large excess (10:1) of MeCN markedly slows the reaction (50% conversion after 48 h at room temperature for N–N = **2**). The same type of π-allylic compound can be obtained by reaction of the square-planar cationic substrates $[PtR(N\text{–}N)(MeCN)]^+$ with DMA.

$$[PtR(N\text{–}N)(MeCN)]^+ + DMA = [Pt(CH_2\text{–}CR\text{–}CMe_2)(N\text{–}N)]^+ + MeCN \quad (4)$$

This reaction reported [8] to occur with cationic *trans*-bis-(phosphine) platinum(II) complexes, is useful synthetically because it can be applied to varieties of R and of N–N ligands (Table 2). In the case of the pyridin-2-imine N–N ligands (**2–4**), which have chemically non-equivalent donor atoms, two geometrical isomers $[Pt(CH_2\text{–}CR\text{–}CMe_2)(N\text{–}N')]^+$ could be obtained, in principle. The two isomers are actually obtained in ca. 1:1 ratio when N–N = **3**, while only one species is detected in the case of the 6-methylpyridinimines (**2** and **4**). It seems reasonable that this isomer is the one having the CMe_2 group *cis* to the imine nitrogen, owing to unfavourable steric interactions that could arise with the six-substituted pyridine ring in the reverse orientation of the π-allylic system. It has already been observed [6a] that such interactions markedly affect the proportions of geometrical isomers of [PtClR(N–N')] complexes.

A conjugated diene such as butadiene (BD) was also used as unsaturated substrate in the reaction with neutral and cationic square-planar PtII complexes. To the best of our knowledge, only one five-coordinate adduct, namely $[\{PtCl_2(dmphen)\}_2(BD)]$ [5b] is known. In this compound, butadiene is η^2-coordinated to two different platinum atoms, both having *tbp* coordination. In our case, mononuclear species [PtClR(BD)(dmphen)] were isolated and characterized (Table 1). BD coordinates through a single double bond, the other being free. Thus, the properties of the compound obtained are very similar to those of five-coordinate platinum(II) complexes with monosubstituted alkenes. As an example, the hindered rotation of the unsaturated ligand around the Pt–BD bond gives rise to two stereoisomers (actually two enantiomeric couples), which are both observed in 1:1 (R = 4-$MeOC_6H_4$) or 7:3 (R = Me) ratios. In the latter case, the ^1H NMR spectrum shows that the Pt-coordinated $=CHCH=CH_2$ proton of the less abundant stereoisomer gives a signal at δ 4.35 ($^2J_{Pt-H}$ = 91 Hz), while the corresponding resonance of the second stereoisomer is at ca. δ 3.4, partially obscured by other signals. Because this shift is attributable to opposing different axial ligands in *tbp* geometry [7], the reported data suggest that the free $CH=CH_2$ group is tilted towards the chlorine atom in the most abundant stereoisomer. The synthesis of five-coordinate adducts was also attempted in the case of **2**. However, we were unable to isolate stable complexes because the dissociative equilibrium (5) is markedly shifted towards the right.

$$[PtClR(BD)(pimpy)] = [PtClR(pimpy)] + BD \quad (5)$$

For example, when R = Me, a nearly equimolar mixture of five- and four-coordinate species is observed at 30°C within a few minutes after the dissolution of the crude solid five-coordinate adduct. This type of behaviour was already observed in the corresponding monosubstituted alkene complexes [6b], the bulkiness of the substituent at the double bond increasing the extent of the olefin release.

Up to four stereoisomers (four enantiomeric couples) should be obtainable for the [PtClMe(BD)(pimpy)] adduct, and they were all detected in the ^1H NMR spectrum. However, only one stereoisomer was predominant (ca. 40%). The presence of several stereoisomers and/or the instability of the five-coordinate adducts towards BD release discouraged us from attempting the synthesis of well-characterized cationic derivatives, by $AgBF_4$ treatment. Instead, four-coordinate $[PtR(N\text{–}N)(MeCN)]^+$ compounds were allowed to react with BD, and the crude reaction products were treated with anhydrous HCl in order to allow isolation and identification of the organic moiety. No reaction was observed when R = Me, while 3-(4-methoxy)phenyl-but-1-ene was formed in the case of R = 4-$MeOC_6H_4$. This behaviour is consistent with that previously reported [1] for simple monosubstituted alkenes.

2.2. Palladium complexes with unsaturated ligands

2.2.1. Alkene ligands

There are few reports [9] on square-planar PdII complexes with η^2-bound unsaturated ligands, because they are usually less stable and/or have a higher reactivity than those of PtII. In addition, a few examples of five-coordinate [PdClMe(olefin)(N–N)] adducts have been described [10]. These were isolated in the solid state only through a careful choice of N–N (e.g. N–N = **1**, see above) and tend to release the olefin in solution. In order to examine their chemical properties, attempts to obtain the cationic species [PdMe(olefin)(dmphen)(MeCN)]$^+$ by a procedure similar to that reported in Eq. 2, were undertaken. The ethylene derivative was identified in solution under C_2H_4 atmosphere to suppress the olefin dissociation equilibrium which is shifted towards the four-coordinate complex $[PdMe(dmphen)(MeCN)]^+$ even more than in the case of the neutral parent compound. This behaviour is very similar to that already observed [11] for the corre-

sponding PtII species. In addition, the presence of a large excess (greater than 10:1) of MeCN is necessary in order to slow the decomposition of the cationic adduct. In fact, in absence of free neutral proligand, palladium black forms and a mixture of dmphen, propene and *E*-2-butene is detected in solution after a few hours. The decomposition process was monitored by ^{1}H NMR spectroscopy (see Experimental details). After 5 h ca. 10% of PdII was reduced to the metal (the evaluation being made on the basis of the free dmphen), while the remainder was present as ca. 1:1 mixture of the starting complex and a new species whose spectral data are consistent with the formula $[PdEt(C_2H_4)(dmphen)(MeCN)]^+$. Propene and *E*-2-butene were also detected in ca. 5:1 ratio, that corresponds reasonably to the ratio [PdO + PdII-Et]/[PdO]. The reaction went to completion within 48 h. The final amount of propene was stoichiometrically comparable with the starting Pd(II) compound, while the *E*-2-butene was higher (ca. 2 equiv.). A possible reaction scheme is shown in Fig. 1.

No traces of 1-butene or *Z*-2-butene were found in the reaction mixture. In addition, when the decomposition process was performed on $[Pd(CD_3)(C_2H_4)(dmphen)(MeCN)]^+$ the label was found only in the propene fraction. Some isotopic scrambling was observed within the propene, and this is consistent with the depicted reversible hydrogen migration/β-elimination process.

As similar results were obtained when the square-planar $[PdMe(dmphen)(MeCN)]^+$ was allowed to stand in solution in presence of ethylene, other four-coordinate cationic species with N–N less crowded than dmphen were tested. Higher alkenes were formed in these cases. For example, when N–N = **6** a mixture of C_6 and C_8 alkenes was obtained.

Some olefins other than ethylene were also tested. We observed that the presence of subtituents on the double bond hinders the oligomerization process. In fact, when propene or styrene were used, a mixture of *E*-2-butene, and 2-methyl-propene or *E*-β-methyl-styrene respectively, were found in stoichiometric yields.

Olefins with electron-withdrawing substituents are unreactive, an exception being the allylic alcohol CH_2=$CHCH_2OH$. In this case, isomerization to propionaldehyde was observed, together with the formation of a small amount of butyraldehyde.

When phenylpalladium species were used, we failed to get a neutral or cationic square-planar [PdXPh(dmphen)] (X = halogen or MeCN). Therefore, the preliminary coordination of olefin to the substrate to form a five-coordinate adduct could not be attempted. The reactions between $[PdPh(bipy)(MeCN)]^+$ and ethylene, propene, and styrene were examined using the experimental conditions described above, and monitoring by ^{1}H NMR spectroscopy.

When gaseous ethylene was added in stoichiometric amount to a nitromethane solution of the above complex, very fast olefin uptake took place and signals attributable to a Pd–CHMePh moiety were observed. This species has a moderate stability because its complete decomposition to palladium black and styrene occured within 24–36 h. On halide addition, a yellow solid having the stoichiometric formula [PdCl(CHMePh)(bipy)] could be isolated, but decomposition within a few minutes occurred in chloroform solution. A possible reaction pattern, accounting for the Pd-bound secondary carbon, is depicted in Fig. 2.

If ethylene is added in excess to the $[PdPh(bipy)(MeCN)]^+$ solution, styrene and *E*-2-butene are observed in the decomposition mixture.

Similar behaviour was observed with propene. In fact, the first reaction product detected in solution

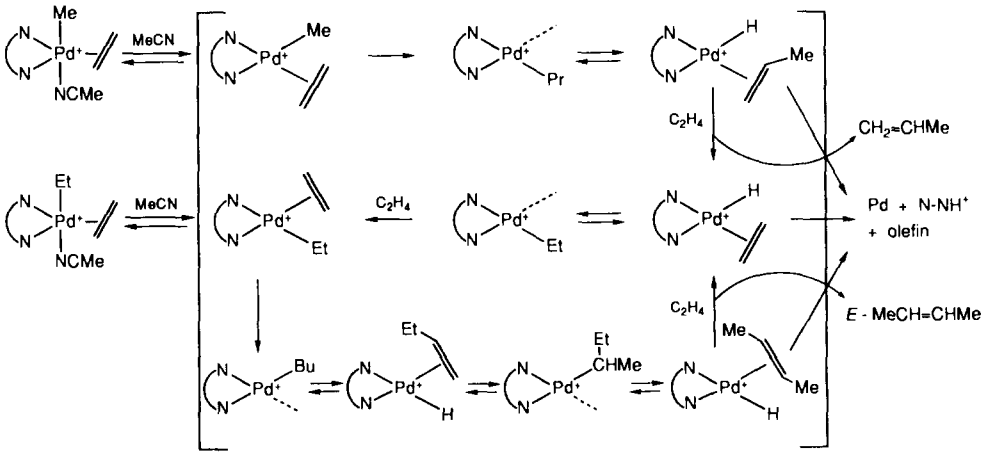


Fig. 1.

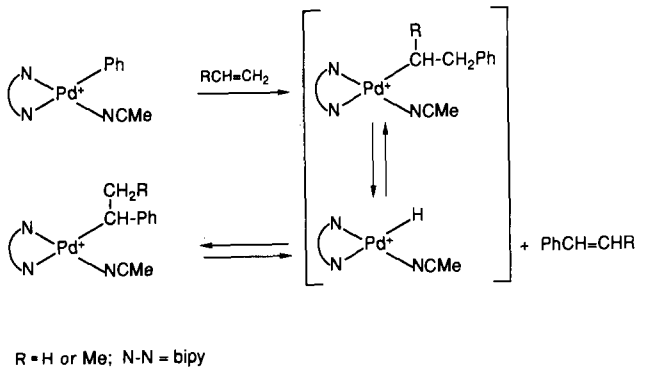


Fig. 2.

showed a Pd–CHEtPh moiety and its decomposition afforded *E*-β-methyl-styrene (Fig. 2).

When styrene was used its uptake was slower and the formation of a Pd–CH(Ph)CH_2Ph moiety was detected. This intermediate decomposed with time. *E*-stylbene was obtained and the same Pd–CHMePh-containing species as above, was formed (Fig. 3).

2.2.2. Alkyne ligands

[PdClMe(dmphen)] and $[PdMe(dmphen)(MeCN)]^+$ were allowed to react with $CF_3C{\equiv}CCF_3$ and MeOOCC≡CCOOMe. No evidence of five-coordinate adducts were found, but the corresponding σ-vinyl derivatives arising from the methyl insertion into the triple bond were isolated.

$$[PdMe(L)(dmphen)] + R'C{\equiv}CR' = [Pd\{C(R')=C(Me)R'\}(L)(dmphen)] \quad (6)$$

L = Cl or MeCN; R' = CF_3 or COOMe

A *cis* arrangement of the Me group to the Pd σ-bound vinyl was inferred by the close similarities with the corresponding Pt complexes [12]. Attempts to isolate the free organic compound were unsuccessful. Similar results were obtained when $[PdPh(bipy)(MeCN)]^+$ was used.

A competing of reductive elimination of MeCl occurs when the neutral metal complexes are used. In this case, appreciable amounts of the three-coordinate [Pd(alkyne)(dmphen)] complexes are isolated in the reaction mixture. This last process predominates if the palladium complex is used in the iodide form.

2.2.3. 1,3-Butadiene (BD) and 3-methyl-1,2-butadiene (DMA)

When an excess of 1,3-butadiene was added to a chloroform solution of [PdClMe(dmphen)], coordination of BD occurred in solution at room temperature. This species could not be isolated in the solid state, because removing the solvent favours the dissociation of the BD and reversion to the parent square-planar complex. However, the ^1H NMR spectra of the reaction mixture suggest a five-coordinate mononuclear adduct. Two rotamers are present in a nearly 2:1 ratio, but structural assignment was not possible. We do not have experimental data to assume ourselves that the criterion used in the case of the corresponding PtII rotamers (see section 2.1.) to assign the orientation of the BD ligand holds in PdII chemistry. In addition, a marked signal overlap is observed in the ^1H NMR spectrum of the PdII–BD complex.

When BD was added to the cationic species $[PdMe(dmphen)(MeCN)]^+$, a π-allyl derivative was isolated in good yield.

$$[PdMe(dmphen)(MeCN)]^+ + BD = [Pd(CH_2{-}CH{-}CHEt)(dmphen)]^+ + MeCN \quad (7)$$

Both *syn* and *anti* isomers were detected in ca. 2:1 ratio. The assignment has been made from the $^3J_{CH-CHEt}$ coupling constant, 13 Hz for the major isomer and ca. 7 Hz for the minor. The diagnostic meaning [13] of this difference is largely accepted.

When an excess of DMA was added to [PdClMe(dmphen)], no five-coordinate adducts could be isolated in the solid state. A relatively fast methyl migra-

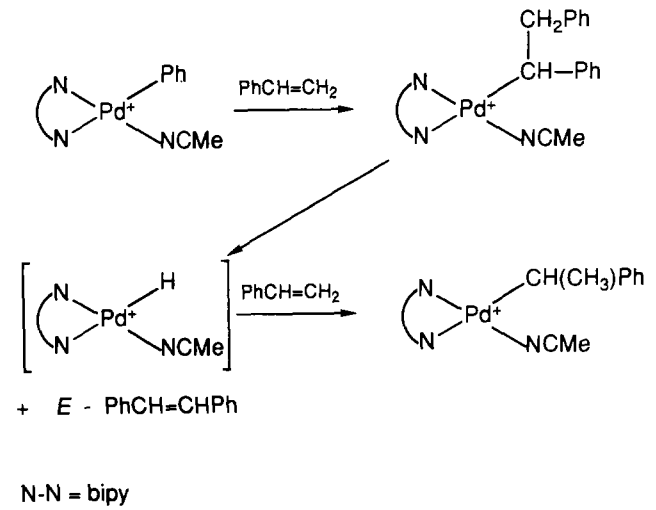


Fig. 3.

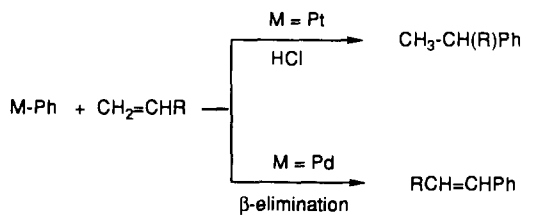


Fig. 4.

tory insertion took place in solution, affording a π-allyl derivative. Similar results with a faster reaction rate were obtained with the cationic [PdMe(dmphen)(MeCN)]$^+$ and [PdPh(bipy)(MeCN)]$^+$.

$$[PdR(N\text{–}N)(MeCN)]^+ + DMA = [Pd(CH_2\text{–}CR\text{–}CMe_2)(N\text{–}N)]^+ + MeCN \quad (8)$$

3. Conclusions

These and earlier results [1,2] on C–C bond formation between a metal-bound hydrocarbyl and an unsaturated ligand indicate that this process is quite general, provided some conditions are fulfilled. A cationic species [MR(L–L)L']$^+$ (M = Pt or Pd; L–L, L' = neutral ligands) seems to be suitable to promote the migratory-insertion reaction in all cases. L' must display a moderate coordinating ability (as in MeCN) in order not to compete with the unsaturated ligand. In addition, chelating L–L favours the attainment of the required [14] *cis* arrangement between the two reacting organic moieties. The expected reactivity orders: Pd > Pt; M-aryl > M-alkyl; 1,2-dienes > alkynes > 1,3-dienes > monoenes, are always observed. In fact, the only case where we did not obtain satisfactory results is the Pt–Me/alkene system [1]. The organic reaction product is recovered as an η^1 or η^3 metal-bound fragment when alkynes or DMA are used. In the alkene case, the differences in the chemical behaviour of corresponding Pt [1] and Pd complexes can be related to the inertness of the Pt–carbyl bond toward β-elimination. With the Pt system, the organic fragment is metal σ-bound in a solid reaction product, and can be freed only by protolysis [1], while an unsaturated organic compound forms spontaneously from the Pd system. Two different organic products are formed, indicating a different regiochemical control from reactions between Pt–Ph [1] and Pd–Ph species with monosubstituted olefins (such as propene and styrene) (see Fig. 4).

While the usually expected Pt–C_α(alkene) bond is formed in the insertion step [1], strong preference for the formation of a Pd–C_β bond is observed. Even in the case of ethylene, styrene does not arise from a β-phenyl–ethyl palladium group. A α-phenyl-ethyl palladium fragment, probably formed through a fast β-elimination/hydride insertion equilibrium (see Fig. 2), is clearly detected in solution. These data indicate that a phenyl group on a Pd-bound carbon exerts a strong stabilizing effect on the corresponding carbyl species. This observation is supported by the results obtained on reaction of a Pd–Me complex with propene and styrene. Only *E*-β-methylstyrene is isolated in the latter case, while a 1:1 mixture of *E*-2-butene and 2-methylpropene is detected in the former. Different reaction mechanisms could explain this reversed regiochemical control on going from Pt to Pd (a radical path could account for the observed Pd–C_β bond). However, we note that the preference to the formation of a Pd–CH(R)Ph group could be simply because of the possibility of a transient η^3 interaction with the organic fragment. In fact, this situation has been already observed [15] in the rearrangement of [CpNiPh(C_2H_4)] (Cp = cyclopentadienyl). As a confirmation, we observe that on reaction of the homologous M–Ph complexes with BD, which is as monodentate, platinum binds to the terminal carbon atom, while internal carbon–Pd bond formation allows the attainment of a more stable η^3 interaction with the organic moiety.

Table 3
Analytical data of selected compounds

Entry	Formula	Anal. Found (Calc.) (%)		
		C	H	N
I	$C_{20}H_{23}ClN_2Pt$	46.1 (46.02)	4.5 (4.44)	5.5 (5.37)
III	$C_{26}H_{27}ClN_2OPt$	51.0 (50.86)	4.5 (4.43)	4.7 (4.56)
IV	$C_{19}H_{21}ClN_2Pt$	45.1 (44.93)	4.2 (4.17)	5.6 (5.52)
V	$C_{25}H_{25}ClN_2OPt$	51.0 (50.04)	4.3 (4.20)	4.7 (4.67)
VI	$C_{19}H_{23}ClN_2Pt$	44.8 (44.75)	4.6 (4.55)	5.6 (5.49)
VIII	$C_{25}H_{27}ClN_2OPt$	50.0 (49.88)	4.6 (4.52)	4.7 (4.65)
X	$C_{20}H_{23}BF_4N_2Pt$	42.0 (41.90)	4.1 (4.04)	4.9 (4.89)
XII	$C_{19}H_{23}BF_4N_2Pt$	40.7 (40.66)	4.2 (4.13)	5.0 (4.99)
XIII	$C_{20}H_{25}BF_4N_2Pt$	41.8 (41.75)	4.4 (4.38)	4.9 (4.87)
XIV	$C_{25}H_{27}BF_4N_2OPt$	46.0 (45.96)	4.2 (4.16)	4.3 (4.29)
XVI	$C_{25}H_{27}BF_4N_2Pt$	47.2 (47.11)	4.3 (4.27)	4.4 (4.39)
XVII	$C_{19}H_{23}BF_4N_2OPt$	39.6 (39.53)	4.1 (4.02)	4.9 (4.85)
XX	$C_{20}H_{23}BF_4N_2Pd$	49.7 (49.57)	4.8 (4.78)	5.8 (5.78)
XXIII	$C_{19}H_{23}BF_4N_2Pd$	48.4 (48.29)	5.0 (4.91)	6.0 (5.93)
XXV	$C_{18}H_{19}BF_4N_2Pd$	47.4 (47.35)	4.3 (4.19)	6.2 (6.14)

4. Experimental details

^{1}H NMR spectra were recorded on a Varian XL-200 or on a Bruker AC-270 spectrometer in $CDCl_3$ solution with $CHCl_3$ as internal standard, or in CD_3NO_2 with CHD_2NO_3 as internal standard. Elemental analyses (see Table 3) were performed with a Carlo Erba 1106 elemental analyzer. GC analyses were made by using a Carlo Erba gas-chromatograph VEGA 6000.

Compounds **1**, **5** and **6** are commercially available, while **2–4** were prepared as previously described [16]. [PtClR(N–N)] and [PtR(N–N)(MeCN)]$^+$ were obtained by adapting known procedures [6,11]. [PdClMe(N–N)] [10] and [PdIPh(tmeda)] [17] (tmeda = *N,N,N',N'*-tetramethyl-1,2-ethanediamine) were synthesized as described. [PdCl(CD_3)(C_2H_4)(dmphen)] was prepared by adapting the procedure used for the corresponding unlabeled complex. Solvents and reagents were of AnalaR grade and were used without further purification, unless otherwise stated.

4.1. Synthesis of [PtClR(DMA)(N–N)] (N–N = 1 or 2; R = Me or 4-MeOC$_6$H$_4$) (I–III, VI–VIII)

An excess DMA was added at room temperature to a solution of 0.5 mmol of the appropriate four-coordinate [PtClR(N–N)] in 5 ml of dichloromethane. After overnight stirring, the mixture was filtered through Celite. Crystallization of the filtrate was achieved by adding diethyl ether. White crystals were obtained in 80–90% yield ^{1}H NMR are in Table 1.

4.2. Synthesis and rearrangement of [PtR(DMA)(N–N)(MeCN)]BF$_4$ (N–N = 1 or 2; R = Me or 4-MeOC$_6$H$_4$)(X–XVI)

An equimolar amount of AgBF$_4$ dissolved in 5 ml of MeCN was added dropwise at 0°C to a solution of 0.5 mmol of the appropriate five-coordinate [PtClR (DMA)-(N–N)] in 10 ml of dichloromethane/methyl cyanide mixture. After 20 min stirring, the mixture was filtered through Celite and the filtrate evaporated to dryness. For R = 4-MeOC$_6$H$_4$, π-allylic complexes were isolated after recrystallization from chloroform/diethyl ether in 85% yield. For R = Me, the crude product was a five-coordinate cationic complex that quantitatively transformed into a π-allylic complex on standing in solution. ^{1}H NMR data are in Table 2.

^{1}H NMR (δ, CDCl$_3$): [PtMe(DMA)(dmphen)-(MeCN)]BF$_4$ (identified in solution), 8.5 (m, 2H), 7.95 (s, 2H), 7.9 (m, 2H), 3.49 (s, 3H, Me), 3.29 (s, 3H, Me), 3.0 (m, 2H, =CH$_2$, $^2J_{PtH}$ = 80 Hz), 2.17 (s, 3H, Me), 2.13 (s, 3H, MeCN), 2.03 (s, 3H, Me), −0.03 (s, 3H, Pt–Me, $^2J_{PtH}$ = 72 Hz);

[PtMe(DMA)(pimpy)(MeCN)]BF$_4$ (identified in solution), 9.20 (s, 1H, $^3J_{PtH}$ = 40 Hz), 8.1 (m, 2H), 7.70 (m, 1H), 7.4(m, 5H), 3.03 (s, 3H, Me), 2.75 and 2.55 (2bs, 2H, =CH$_2$), 2.18 (s, 3H, Me), 2.10 (s, 3H, MeCN), 1.93 (s, 3H, Me), 0.20 (s, 3H, Pt–Me, $^2J_{PtH}$ = 73 Hz).

4.3. Reaction of [PtR(N–N)(MeCN)]BF$_4$ with DMA (N–N = 1–5)

To a solution of 0.5 mmol of the title complexes in 10 ml of dichloromethane/methyl cyanide mixture 4–5 equivalents of DMA were added. After 12–24 h stirring at room temperature, the mixture was filtered through Celite and the filtrate evaporated to dryness. The π-allylic complexes were isolated after recrystallization from chloroform/diethylether in 80% yield. ^{1}H NMR data are in Table 2.

4.4. Synthesis of [PtClR(BD)(N–N)] (N–N = 1 or 2; R = Me, or 4-MeOC$_6$H$_4$)(IV, V and IX)

BD was bubbled at 0°C for 3 min through a solution of 0.5 mmol [PtClR(N–N)] in 15 ml of dichloromethane. After 12 h stirring at room temperature, the product was precipitated by adding diethyl ether to the Celite filtered solution. The five-coordinate products were obtained as microcrystalline yellow solids. Yields: 80–85%. ^{1}H NMR data are in Table 1.

4.5. Reaction of [Pt(4-MeOC$_6$H$_4$)(pimpy)(MeCN)]BF$_4$ with BD

BD was bubbled at 0°C for 3 min through a solution of 0.5 mmol of the four-coordinate cationic complex in 15 ml of dichloromethane/nitromethane. After 24 h stirring at room temperature, the mixture was worked up as previously described [1]. The organic product was isolated and identified [18] as 4-MeOPhCH(Me)–CH=CH$_2$: ^{1}H NMR (δ, CDCl$_3$): 7.15 (d, 2H), 6.85 (d, 2H), 6.0 (m, 1H, CH=), 5.0 (m, 2H, =CH$_2$), 3.79 (s, 3H, OMe), 3.4 (m, 1H, CH), 1.32 (d, 3H, Me).

4.6. Synthesis of [PdIPh(bipy)]

0.213 g (0.5 mmol) of [PdIPh(tmeda)] and 0.156 g (1 mmol) of bipy were dissolved in 10 ml of dichloromethane. 20 μl of a 1:100 v/v dichloromethane solution of trifluoroacetic acid were added. After 24 h, orange crystals of the product were collected in a nearly quantitative yield. Anal. Found: C, 41.2; H, 2.9; N, 5.85. C$_{16}$H$_{13}$IN$_2$Pd, Calc.: C, 41.19; H, 2.81; N, 6.00%. ^{1}H NMR (δ, CDCl$_3$): 9.62 (d, 1H, 6-H-bipy), 8.05 (m, 4H), 7.75 (d, 1H), 7.50 (m, 1H), 7.35 (m, 1H), 7.25 (m, 2 Ph–H), 6.75 (m, 3 Ph–H).

4.7. Synthesis of [PdMe(C$_2$H$_4$)(dmphen)(MeCN)]BF$_4$, [PdCD$_3$(C$_2$H$_4$)(dmphen)(MeCN)]BF$_4$ and [PdR(N–N)(MeCN)]BF$_4$ (R = Me or Ph)

One molar equivalent of AgBF$_4$ dissolved in 5 ml of methyl cyanide was added dropwise at 0°C to a solution of 0.5 mmol of the appropriate neutral complex in 10 ml of dichloromethane. After 20 min stirring, the mixture was filtered through Celite and the filtrate evaporated to dryness in the case of the tetracoordinate species, while the five coordinate complexes were recovered on adding hexane in presence of ethylene. The ionic complexes were obtained as white-to-pale yellow powders in 70–90% yield.

[PdMe(C$_2$H$_4$)(dmphen)(MeCN)]BF$_4$: Anal. Found: C, 46.8; H, 4.4; N, 8.8. C$_{19}$H$_{22}$BF$_4$N$_3$Pd Calc.: C, 46.99; H, 4.57; N, 8.65%. ^{1}H NMR (δ, CDCl$_3$): 8.42 (d, 2H), 7.91 (s, 2H), 7.82 (d, 2H), 4.10 (broad, 2H, C$_2$H$_4$), 3.55 (broad, 2H, C$_2$H$_4$), 3.19 (s, 6H, 2 Me), 2.3 (s, 3H, MeCN), 0.42 (s, 3H, Pd–Me).

[PdMe(dmphen)(MeCN)]BF$_4$: Anal. Found: C, 44.6; H, 3.8; N, 9.05, C$_{17}$H$_{18}$BF$_4$N$_3$Pd Calc.: C, 44.63; H, 3.97; N, 9.18%. ^{1}H NMR (δ, CDCl$_3$): 8.49 (d, 2H), 7.94 (s, 2H), 7.80 (d, 2H), 2.94 (s, 6H, 2 Me), 2.19 (s, 3H, MeCN), 1.10 (s, 3H, Pd–Me).

[PdMe(bipy)(MeCN)]BF_4: Anal. Found: C, 38.6; H, 3.4; N, 10.3. $C_{13}H_{14}BF_4N_3Pd$ Calc.: C, 38.51; H, 3.48; N, 10.36%. ^1H NMR (δ, $CDCl_3$): 8.65 (m, 2H), 8.40 (m, 2H), 8.25 (m, 2H), 7.70 (m, 2H), 2.60 (s, 3H, MeCN), 1.03 (s, 3H, Pd–Me).

[PdMe(phen)(MeCN)]BF_4: Anal. Found: C, 42.1; H, 3.3; N, 9.8. $C_{15}H_{14}BF_4N_3Pd$ Calc.: C, 41.95; H, 3.29; N, 9.78%. ^1H NMR (δ, $CDCl_3$): 8.85 (m, 2H), 8.70 (m, 2H), 8.10 (s, 2H), 8.0 (m, 2H), 2.63 (s, 3H, MeCN), 1.14 (s, 3H, Pd–Me).

[PdPh(bipy)(MeCN)]BF_4: Anal. Found: C, 46.1; H, 3.3; N, 8.7. $C_{18}H_{16}BF_4N_3Pd$ Calc.: C, 46.24; H, 3.45; N, 8.99%. ^1H NMR (δ, $CDCl_3$): 8.70 (d, 1H, 6-H-bipy), 8.30 (m, 4H), 7.90 (d, 1H), 7.80 (m, 1H), 7.50 (m, 1H), 7.40 (m, 2 Ph–H), 7.15 (m, 3 Ph–H), 2.51 (s, 3H, MeCN).

4.8. Monitoring of the reaction between [PdMe(C_2H_4)-(dmphen)(MeCN)]BF_4 and ethylene

Experimental conditions: [PdMe(C_2H_4)(dmphen)-(MeCN)]BF_4 0.1 M, solvent $CDCl_3/CD_3CN$, complex/CD_3CN ratio 1:10, room temperature, C_2H_4 atmosphere. 5 h after dissolving the solids, the ^1H NMR spectra showed the presence of the dmphen (ca.10%), the starting complex (45%) and a new palladium complex (45%) that was assumed to be [PdEt(C_2H_4)(dmphen)(MeCN)]$^+$: δ 8.45 (d, 2H), 7.90 (s, 2H), 7.85 (d, 2H), 4.10 and 3.50 (br, C_2H_4), 3.25 (s, 6H, 2 Me), 1.50 (q, 2H, Pd–CH_2), 0.01 (t, 3H, Me). Propene and *E*-2-butene were also detected. The reaction went to completion within 48 h. The identification of the olefins was made by comparing the ^1H NMR spectrum of the reaction mixture with the spectra of authentic samples in the same solvent at a comparable concentration. In addition, the reaction mixture was trap-to-trap distilled, and analyzed by gas chromatography with a 30 m SPB-5 capillary column.

4.9. General procedure of the reaction between [PdMe(N–N)(MeCN)]BF_4 and olefins

0.1 mmol of complex was dissolved in 2 ml of CD_3NO_2. An excess (5:1) of the olefin was added at room temperature. Gaseous olefin was bubbled into the solution. After a few minutes palladium black formed, leaving a clear solution that was analyzed by ^1H NMR spectroscopy. Identification of the organic products was made by comparison with authentic samples.

4.10. Monitoring of the reaction between [PdPh(bipy)-(MeCN)]BF_4 and olefins (ethylene, propylene or styrene)

0.1 mmol of complex were dissolved in 1 ml of CD_3NO_2. An almost stoichiometric amount of the olefin was added at room temperature as a liquid or by a gas syringe.

Ethylene: fast olefin uptake and formation of a new palladium complex that was assumed to contain the Pd–CH(Me)Ph moiety: δ 8.95 (d, 1H, 6-Hbipy), 8.4–7.6 (m, Hbipy and HPh), 4.00 (q, 1H, Pd–CH), 1.50 (d, 3H, Me). The solution was concentrated to dryness and the solid residue was dissolved in 5 ml of acetone. Solid LiCl was added and the mixture was stirred for 30 min. After filtering through Celite, the solvent was removed in vacuo. A yellow powder was obtained that was identified as [PdCl(CHMePh)(bipy)]. Anal. Found: C, 53.4; H, 3.1; N, 6.7. $C_{18}H_{17}ClN_2Pd$ Calc.: C, 53.62; H, 4.25; N, 6.95%. ^1H NMR (δ, $CDCl_3$): 9.00 (br, 1H, 6-Hbipy), 8.1–7.1 (m, 12H), 4.70 (q, 1H, Pd–CH), 1.22 (d, 3H, Me). Decomposition of this species gave styrene, identified as above.

Propylene: fast olefin uptake and formation of a new palladium complex that was assumed to contain the Pd–CH(Ph)CH_2Me moiety: δ 8.9 (br, 1H, 6-Hbipy), 8.6–7.1 (m, Hbipy and HPh), 4.10 (dd, 1H, Pd–CH), 2.10 (m, 2H, CH_2), 1.30 (t, 3H, Me). This species eliminates *E*-β-methylstyrene, identified as above.

Styrene: fast olefin uptake and formation of a new palladium complex that was assumed to contain the Pd–CH(Ph)CH_2Ph moiety: δ 8.6 (br, 1H, 6-Hbipy), 8.4–7.1 (m, Hbipy and HPh), 4.50 (dd, 1H, Pd–CH), 3.10 (m, 2H, CH_2). This species eliminates *E*-stylbene and after 30 min resonances attributed to the Pd–CH(Me)Ph moiety were observed.

4.11. Reaction of [PdClR(N–N)] with DMA

To a solution of 0.5 mmol of [PdClR(N–N)] in 10 ml of dichloromethane, DMA (0.6 mmol, a 10% excess) was added. After 5 min (or 24 h when N–N = **4**) the solvent was evaporated to leave the π-allylic complex in 80–90% yield. ^1H NMR data are in Table 2.

4.12. Reaction of [PdR(N–N)(MeCN)]BF_4 complexes with DMA

To a solution of 0.5 mmol of [PdR(N–N)(MeCN)]BF_4 in 10 ml of dichloromethane/nitromethane (3:1 v/v) DMA (0.6 mmol: a 10% excess) was added. After 5 min the solvent was evaporated to leave the π-allylic complex in 80–90% yield. ^1H NMR data are in Table 2.

4.13. Reaction of [PdClMe(dmphen)] complex with BD

0.015 g (0.04 mmol) of [PdClMe(dmphen)] were dissolved in 0.5 ml of $CDCl_3$ and a large excess of BD (20:1) was added. A mixture of two five-coordinate complexes (isomer A 67%, isomer B 33%) was immediately detectable. ^1H NMR (δ, $CDCl_3$): isomer A 8.25 (d, 2H), 7.80 (s, 2H), 7.69 (d, 2H), 6.84 (m, 1H, =CH

not coordinated), 5.50 (dd, 1H, =CH_2 not coordinated), 5.38 (dd, 1H, =CH_2 not coordinated), 4.53 (m, 1H, =CH), 4.38 (d, 1H, =CH_2), 3.56 (d, 1H, CH_2), 3.35 (s, 3H, Me), 3.30 (s, 3H, Me), 0.40 (s, 3H, Pd–Me); isomer B 8.22 (d, 2H), 7.78 (s, 2H), 7.60 (d, 2H), 6.63 (m, 1H, =CH not coordinated), 3.38 (s, 3H, Me), 3.34 (s, 3H, Me), 0.46 (s, 3H, Pd–Me).

4.14. Reaction of [PdMe(dmphen)(MeCN)]BF_4 with BD

0.229 g (0.5 mmol) of [PdMe(dmphen)(MeCN)]BF_4 were dissolved in 10 ml of dichloromethane/nitromethane (3:1 v/v) and BD was bubbled through at 0°C for 3 min. After 1 h stirring at 0°C, the solution was filtered through Celite and the solvent was removed under vacuum. The π-allylic complex was obtained with a yield of 80%. ^{1}H NMR (δ, $CDCl_3$/CD_3NO_2): *syn* isomer (66%) 8.58 (d, 2H), 8.02 (s, 2H), 7.90 (d, 2H), 5.60 (d app t, 1H, H_2), 4.70 (d, 1H, H_{1s}), 4.56 (m, 1H, H_{3a}), 3.65 (d, 1H, H_{1a}), 3.11 (s, 6H, 2 Me), 1.88 (m, 2H, CH_2), 1.11 (t, 3H, CH_3); *anti* isomer (33%) 8.60 (d, 2H), 8.06 (s, 2H), 7.95 (d, 2H), 5.78 (m, 1H, H_2), 3.09 (s, 6H, 2 Me), 1.00 (t, 3H, CH_3).

4.15. Reaction of [PdClMe(dmphen)] with RC≡CR (R = CF_3 or COOMe)

0.180 g (0.5 mmol) of [PdClMe(dmphen)] were dissolved in 10 ml of dichloromethane. An excess of the alkyne was added at 0°C ($CF_3C{\equiv}CCF_3$ was bubbled for 3 min; 70 μl of MeOOCC≡CCOOMe were added). After 10 min the solvent was removed under vacuum. The crude reaction product was purified by chromatography on Florisil and eluting with dichloromethane.

[PdCl{C(CF_3)=CMe(CF_3)}(dmphen)] (45% yield): Anal. Found: C, 43.2; H, 2.9; N, 5.2. $C_{19}H_{15}ClF_6N_2Pd$ Calc.: C, 43.29; H, 2.87; N, 5.31%. ^{1}H NMR (δ, $CDCl_3$): 8.35 (d, 1H), 8.27 (d, 1H), 7.84 (s, 1H), 7.83 (s, 1H), 7.61 (d, 1H), 7.58 (d, 1H), 3.27 (s, 3H, Me), 2.81 (s, 3H, Me), 2.42 (q, 3H, Me, $^4J_{H-F}$ = 4 Hz); [Pd($CF_3C{\equiv}CCF_3$)(dmphen)] (45% yield): Anal. Found: C, 45.3; H, 2.5; N, 5.9. $C_{18}H_{12}F_6N_2Pd$ Calc.: C, 45.35; H, 2.54; N, 5.88%. ^{1}H NMR (δ, $CDCl_3$): 8.30 (d, 2H), 7.82 (s, 2H), 7.75 (d, 2H), 3.15 (s, 6H, 2 Me).

[PdCl{C(COOMe)=CMe(COOMe)}(dmphen)] (25% yield). Anal. Found: C, 49.6; H, 4.1; N, 5.5. $C_{21}H_{21}ClN_2O_4Pd$ Calc.: C, 49.72; H, 4.17; N, 5.52%. ^{1}H NMR (δ, $CDCl_3$): 8.29 (d, 1H), 8.22 (d, 1H), 7.79 (s, 1H), 7.78 (s, 1H), 7.66 (d, 1H), 7.51 (d, 1H), 3.64 (s, 3H, OMe), 3.55 (s, 3H, OMe), 3.20 (s, 3H, Me), 2.95 (s, 3H, Me), 2.61 (s, 3H, Me).

[Pd(MeOOCC≡CCOOMe)(dmphen)] (50% yield). Anal. Found: C, 52.5; H, 3.9; N, 6.0. $C_{20}H_{18}N_2O_4Pd$ Calc.: C, 52.59; H, 3.97; N, 6.13%. ^{1}H NMR (δ, $CDCl_3$): 8.23 (d, 2H), 7.73 (s, 2H), 7.58 (d, 2H), 3.83 (s, 6H, 2 OMe), 3.07 (s, 6H, 2 Me).

4.16. Reaction of [PdMe(dmphen)(MeCN)]BF_4 with MeOOCC≡CCOOMe

0.228 g (0.5 mmol) of the complex were dissolved in 5 ml of nitromethane. A slight excess of the alkyne was added. After a few minutes the solvent was removed leaving a yellow powder.

Pd{C(COOMe)=CMe(COOMe)}(dmphen)(MeCN)]BF_4 (85% yield). Anal. Found: C, 46.1; H, 4.1; N, 7.1. $C_{23}H_{24}BF_4N_3O_4Pd$ Calc.: C, 46.07; H, 4.03; N, 7.01%. ^{1}H NMR (δ, CD_3NO_2): 8.59 (d, 2H), 8.02 (s, 2H), 7.83 (d, 2H), 3.70 (s, 3H, OMe), 3.57 (s, 3H, OMe), 3.01 (s, 6H, 2 Me), 2.54 (br s, 3H, MeCN), 2.37 (s, 3H, Me).

4.17. Reaction of [PdPh(bipy)(MeCN)]BF_4 with MeOOCC≡CCOOMe

A similar procedure to that above was used.

[Pd{C(COOMe)=CPh(COOMe)}(bipy)(MeCN)]BF_4 (85% yield). Anal. Found: C, 47.2; H, 3.6; N, 6.7. $C_{24}H_{22}BF_4N_3O_4Pd$ Calc.: C, 47.28; H, 3.64; N, 6.89%. ^{1}H NMR (δ, CD_3NO_2): 8.83 (d, 1H, 6-Hbipy), 8.53 (d, 1H, 6'-Hbipy), 8.3 (m, 4H), 7.7 (m, 4H), 7.25 (m, 3H), 3.85 (s, 3H, OMe), 3.75 (s, 3H, OMe), 2.64 (s, 3H, MeCN).

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