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Journal of Organometallic Chemistry 577 (1999) 257–264

Journal of Organometallic Chemistry

Syntheses and spectroscopic characteristics of dialkylpalladium(II) complexes; PdR_2(cod) as precursors for derivatives with N- or P-donor ligands

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Received 14 September 1998

Abstract

Cycloocta-1,5-diene dialkylpalladium(II) derivatives, PdR_2(cod), ($R = CH_2SiMe_3$, CH_2SiMe_2Ph) have been isolated and used conveniently as precursors in the preparation of dialkylpalladium complexes, PdR_2L_2, with N- or P-donor ancillary ligands ($R = CH_2SiMe_3$; L_2 = bipy, phen, dppp, dpkt or tmen; $L = PMe_3$; $R = CH_2SiMe_2Ph$; L_2 = bipy; dpkt). The complexes $Pd(CH_2CMe_2Ph)_2$(dppe) and $PdMe_2$(bipy) were also prepared from their cyclooctadiene analogues. All have been characterized by ^1H-, ^{13}C- and ^{31}P-NMR and IR spectroscopy. © 1999 Published by Elsevier Science S.A. All rights reserved.

Keywords: Palladium; Alkylpalladium; Organometallic; Ligand-exchange

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1. Introduction

Recently, we have sought to explore the unusual reactivity of heteromethyl platinum(II) complexes, *cis*-$Pt(CH_2YRR'_n)_2L_2$ and *cis*-$Pt(CH_2YRR'_n)(R'')L_2$ [R, R′, R″ = (variously) alkyl, alkenyl, alkynyl or aryl; Y = Si, Ge, Sn, $n = 2$; Y = S, $n = 0$; L = phosphine] [1–4]. Among these rearrangements, the most singular, perhaps, are the β-carbon migrations exhibited by sila-alkyl [1] and germa-alkyl [2] derivatives of platinum. We were interested in evaluating the incidence of this mode of thermolytic reactivity for corresponding complexes of other metals including, quite naturally, nickel [5] and palladium. This has led us to explore new synthetic approaches to such dialkylpalladium(II) species, on which we report here.

Because of the catalytic importance of the metal and its derivatives, alkylpalladium chemistry has proliferated greatly, as reflected in texts [6] and compendious reviews [7]. The main synthetic methods feature direct transalkylations on appropriate carboxylato- or halopalladium(II) species, with the target ancillary ligands already in place or available in situ [7,8]. Platinum complexes of the type, PtR_2(cod), (cod = cycloocta-1,5-diene) are often readily accessible. These have been used frequently as precursors to further organoplatinum(II) derivatives, via displacement of the labile diene [9]. The same has not been true for their palladium analogues (although substitution of certain labile N-donor ligands has been developed recently as a synthetic counterpart [10,11]). Thus, $PdMe_2$(cod), which was among the earliest organopalladium(II) complexes to be reported [12], remains the only characterized dialkylpalladium compound of its class [13] and only a few examples of the related monohalopalladium(II) type—for instance, Pd(Me)Cl(cod) [13], $Pd[CH(SiMe_3)$-$PMe_2Ph]Cl$(cod) [14] and $Pd(C_6F_5)Cl$(cod) [15]—precede the present work. The lability of these complexes might stem in part from the high (Pd–alkene bond-weakening) *trans*-influence of the σ-hydrocarbyl ligands [16].

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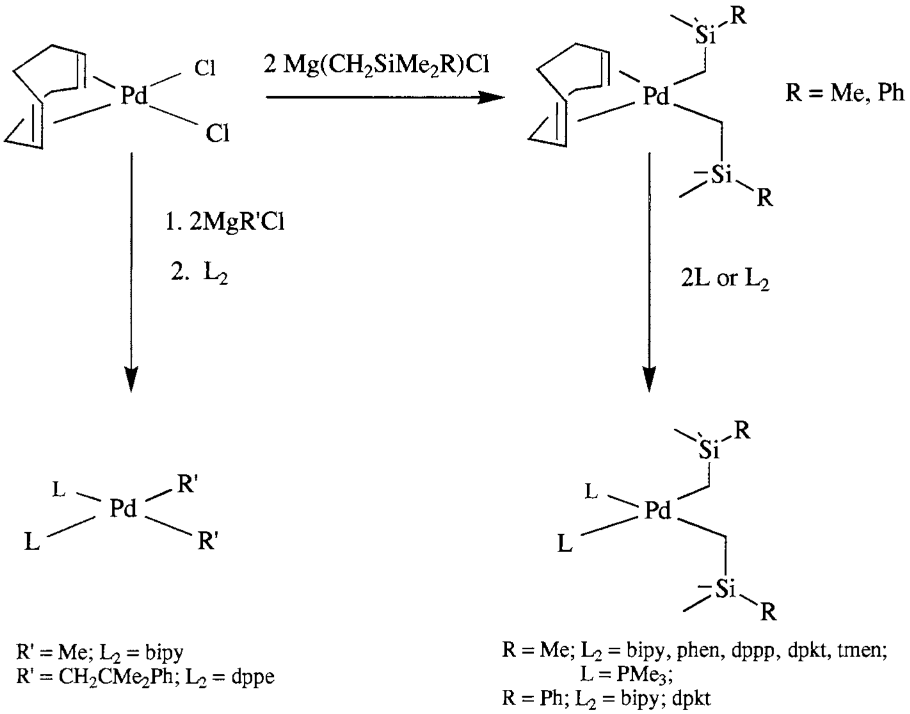
PII: S0022-328X(98)01071-7



Scheme 1.

In the course of our own studies, we have recently accumulated ample evidence that the heteromethyl groups, which interest us, exert substantially smaller *trans*-influences than those of their β-carbon analogues, $CH_2CRR'_2$ [1–4,17]. Employing two such ligands, we now report on the isolation and characterization of two new dialkylpalladium(II) species, $Pd(CH_2SiMe_3)_2(cod)$ and $Pd(CH_2SiMe_2Ph)_2(cod)$, both of which are sufficiently robust to allow their convenient use as precursors to families of dialkylpalladium(II) complexes with P- and N-donor ligands, PdR_2L_2 (Scheme 1) [$R = CH_2SiMe_3$, $L_2 =$ 2,2′-bipyridyl (bipy), 1,10-phenanthroline (phen), 1,3-bis(diphenylphosphino)propane (dppp), di(2-pyridyl)ketone (dpkt), $(Me_2NCH_2)_2$ (tmen), $L = PMe_3$; $R = CH_2SiMe_2Ph$, $L_2 =$ bipy, dpkt]. As a confirmation of the generality of this approach, two other palladium complexes—the known $PdMe_2(bipy)$ [12,13] and a new derivative, $Pd(CH_2CMe_2Ph)_2(dppe)$ [dppe = 1,2-bis(diphenylphosphino)ethane] —were also prepared from corresponding $PdR_2(cod)$, prepared in situ (Scheme 1). All the new compounds have been fully characterized by ^1H-, ^{13}C- and ^{31}P-NMR spectroscopy, IR spectroscopy and by satisfactory elemental analyses.

As has emerged from our investigations, the major thermolytic preference for *cis*-$Pd(CH_2SiMe_3)_2(PMe)_2$ is reductive C–C elimination, generating $Me_3SiCH_2CH_2SiMe_3$. This is in contrast to the unusual reactivity of its platinum analogue [1] but is in broad accord with established patterns of behaviour for many *cis*-dialkylpalladium(II) complexes [7b,18]. A detailed mechanistic analysis of the rearrangement of *cis*-$Pd(CH_2SiMe_3)_2(PMe)_2$ will appear in due course [19].

2. Results and discussion

2.1. Synthesis

Alkylations of $PdCl_2(cod)$ using $Mg(CH_2SiMe_3)Cl$ or $Mg(CH_2SiMe_2Ph)Cl$ were performed in diethylether at low temperature and proceeded very smoothly, to afford clear colorless solutions. Although it is essential to carry out the alkylation under an atmosphere of inert gas and to maintain the temperature below −10°C throughout alkylation, $Pd(CH_2SiMe_3)_2(cod)$ and $Pd(CH_2SiMe_2Ph)_2(cod)$ were isolated as relatively thermolytically and oxidatively inert crystals in high yields. As dry solids, these compounds survive for several hours at ambient temperature in air, without evidence of decomposition. At −20°C under argon, they may be stored indefinitely.

Ligand exchange between $Pd(CH_2SiMe_3)_2(cod)$ or $Pd(CH_2SiMe_2Ph)_2(cod)$ and N- or P- donor ligands has proved to be an extremely facile, effectively instantaneous process—much more rapid than for their platinum analogues [3a–c]. Yields are, generally, almost quantitative. An exception is the reaction between $Pd(CH_2SiMe_3)_2(cod)$ and tetramethylethylenediamine, for which prolonged reaction time and, in consequence, very low temperatures were necessary. Synthesis of

$Pd(CH_2SiMe_3)_2(PMe_3)_2$ by this route afforded the *cis*-isomer as the sole product. This contrasts with the direct alkylation of palladium acetate in the presence of PMe_3, which resulted in only the *trans*-isomer [8]. In a similar fashion, however, *cis*-$PdMe_2(PMePh_2)_2$ is the only product of amine displacement from $PdMe_2$(tmen) by the requisite phosphine [10]. Dipyridylketone was also found to readily replace the diene and $Pd(CH_2SiMe_3)_2$(dpkt) and $Pd[CH_2SiMe_2Ph]_2$(dpkt) were isolated in almost quantitative yields. The susceptibility of the carbonyl group towards nucleophilic addition would preclude syntheses of these derivatives by transalkylations of $PdCl_2$(dpkt).

These ligand-substitution reactions may also be carried out without isolation of the diene complexes. This may be convenient in cases where PdR_2(cod) is more thermolytically labile than is the case for the sila-alkylpalladium precursors. By way of illustration, both $PdMe_2$(bipy) and $Pd(CH_2CMe_2Ph)_2$(dppe) were obtained in high yields using $PdCl_2$(cod) as precursor. In these instances, quenching of excess Grignard reagent was achieved conveniently by addition of acetone to the reaction mixture prior to introduction of the new ligand.

2.2. Spectroscopic characteristics

2.2.1. ^1H-NMR spectroscopy

^1H-NMR data are presented in Table 1. For the phenyldimethylsilylmethyl (sila-neophyl) ligand, a single prime denotes numbering associated with the Si-bonded phenyl group.

The methylene hydrogens of both silylmethyl ligands resonate characteristically to high field, in the range of 0.9 to -0.2 ppm, dependent on the nature of the ancillary ligands. Despite their remoteness, the chemical shifts attributable to the silicon-bound methyl hydrogens are also sensitive to the auxiliary ligands. Relative to the trimethylsilylmethyl ligand, the sila-neophyl group induces a noticeable upfield shift in signals associated with the ancillary ligand. This net shielding might be a result of the anisotropic magnetic influence of the aromatic ring (although a corresponding effect is not immediately evident in ^{13}C-NMR spectra; see below and Table 2).

2.2.2. ^{13}C-, ^{31}P-NMR and IR spectroscopy

$\{^1H\}^{13}C$- and $\{^1H\}^{31}P$-NMR data appear in Table 2. For silylmethyl ligands, palladium-bound carbon resonates upfield from 12 ppm. The most notable upfield shifts for these carbons are associated with heteroaromatic N-donor ancillary ligands. For P-donor ancillary ligands, these carbons generate doubled doublet patterns, as a result of the coupling to both ^{31}P nuclei. ^{31}P-NMR spectra of these phosphorus-containing compounds were also recorded; all generate singlets.

IR data for each complex are listed in the experimental section. For silicon-containing compounds, ν(Si–C) vibrations are apparent at ca. 830 cm^{-1}. Characteristic ν(Pd–C) modes were observed at ca. 530 cm^{-1} in most cases.

3. Experimental

3.1. General procedure

All manipulations were performed under purified dinitrogen. Solvents were heated under reflux with sodium-benzophenone and distilled under dinitrogen prior to use. NMR spectra were recorded on Bruker AM500 (^1H, 500.15 MHz), Bruker WM250 (^1H, 250.13 MHz; ^{13}C, 62.9 MHz), and JEOL FX90Q (^1H, 89.55 MHz; ^{31}P, 36.21 MHz) instruments. IR spectra were collected on a Perkin-Elmer 683 spectrophotometer as Nujol mulls on KBr plates. Elemental analyses were by Imperial College Microanalysis Laboratory.

Cycloocta-1,5-diene, 2,2′-bipyridyl, 1,10-phenathroline, di(2-pyridyl)ketone, 1,2-bis(diphenylphosphino)-ethane and 1,3-bis(diphenylphosphino)propane were all obtained from Aldrich Chemical Co. and were used as supplied. Trimethylphosphine was supplied by Strem Chemicals and was stored under dinitrogen. The compounds chloromethyltrimethylsilane, chloromethyldimethyl-phenylsilane and 1-chloro-2-methyl-2-phenylpropane (neophyl chloride) were obtained from Aldrich Chemical Co. and were distilled prior to use. The compound MgMeCl was supplied as a 1.0 M solution in THF by Aldrich Chemical Co. and was used as supplied.

Diethyl ether solutions of $Mg(CH_2SiMe_3)Cl$ [3a] $Mg(SiCH_2Me_2Ph)Cl$ [3b] and $Mg(CH_2CMe_2Ph)Cl$ [20] were prepared with flame-activated magnesium by previously published methods. The compound $PdCl_2$(cod) was also synthesized according to a published procedure [21].

3.2. Preparation of bis(trimethylsilylmethyl)-(cycloocta-1,5-diene)palladium(II) (**1**)

A solution of $Mg(CH_2Si\ Me_3)Cl$ in diethyl ether (7 ml, 0.45 M, 3.2 mmol) was added to a stirred suspension of $PdCl_2$(cod) (0.29 g, 1 mmol) in the same solvent (30 ml) at -78°C. The mixture was allowed to warm to about -10°C and stirred at that temperature for 30 min, after which all volatiles were removed in vacuo. At no time thereafter were temperatures of dissolved products allowed to exceed -10°C. The residue was extracted with chilled, degassed *n*-hexane (2 × 30 ml) and the combined hexane filtrates were again evaporated to dryness in vacuo. Chilled, degassed acetone (ca. 30 ml) was added to the residue. After filtration, the solution

Table 1
^{1}H-NMR characteristics of PdR_2L_2[a]

Compounds	$C\underline{H}_2Pd$	$SiC\underline{H}_3$	Other ^{1}H: δ /ppm(assignment)
1. $Pd(CH_2SiMe_3)_2(cod)$[b]	0.67(s)	0.28(s)	5.09 (s, br, 4H, =CH), 1.90 (s, br, 8H, CH_2)
2. $Pd(CH_2SiMe_2Ph)_2(cod)$	0.88(s)	0.55(s)	7.69–7.72 (m, 4H, $H_{2'}$), 6.99–7.26 (m, 6H, $H_{3',\ 4'}$), 4.81 (s, br, 4H, =CH), 1.65 (s, br, 8H, CCH_2)
3. $Pd(CH_2SiMe_3)_2(bipy)$	0.08(s)	−0.03(s)	8.82 (dd, $J_{H6\text{–}H5}$ 5.27, $J_{H6\text{–}H4}$ 1.0, 2H, H_6), 8.46 (dd, $J_{H3\text{–}H4}$ 7.92, $J_{H3\text{–}H5}$ 0.99, 2H, H_3), 8.17 (ddd, $J_{H4\text{–}H5}$ 7.58, 2H, H_4), 7.71 (ddd, 2H, H_5)
4. $Pd(CH_2SiMe_3)_2(phen)$	0.24(s)	−0.02(s)	9.16 (dd, $J_{H2\text{–}H3}$ 4.95, $J_{H2\text{–}H4}$ 1.32, 2H, H_2), 8.77 (dd, $J_{H4\text{–}H3}$ 8.25, $J_{H4\text{–}H2}$ 1.65, 2H, H_4), 8.17 (s, 2H, H_5), 8.06 (dd, 2H, H_3)
5. $Pd(CH_2SiMe_3)_2(dpkt)$	−0.13(s)	−0.13(s)	8.81 (ddd, $J_{H6\text{–}H5}$ 5.28, $J_{H6\text{–}H4}$ 1.65, $J_{H6\text{–}H3}$ 0.66, 2H, H_6), 8.46 (ddd, $J_{H3\text{–}H4}$ 7.59, $J_{H3\text{–}H5}$ 1.65, 2H, H_3), 8.19 (ddd, $J_{H4\text{–}H5}$ 7.76, 2H, H_4), 7.80 (ddd, 2H, H_5)
6. $Pd(CH_2SiMe_3)_2(dppp)$	0.24(d, br, $J_{P\text{–}H}$ 5.0)	−0.22(s)	7.56–7.63 (m, 8H, $H_{2,\ 6}$), 7.37–7.41 (m, 12H, $H_{3,\ 4,\ 5}$), 2.50–2.57 (m, 4H, CH_2P), 1.72–1.98 (m, 2H, CH_2CP)
7. *cis*-$Pd(CH_2SiMe_3)_2(Pme_3)_2$	0.49(dd, J^{cis}5.5, J^{trans}10.7)	0.32(s)	0.88 (d, $J_{P\text{–}H}$ 6.56, CH_3P)
8. $Pd(CH_2SiMe_3)_2(tmen)$	−0.11(s)	0.47(s)	1.92 (s, 12H, NCH_3), 1.52 (s, 4H, NCH_2)
9. $Pd(CH_2SiMe_2Ph)_2(bipy)$	0.31(s)	0.24(s)	8.62 (dd, $J_{H6\text{–}H5}$ 5.28, $J_{H6\text{–}H4}$ 1.59, 2H, H_6), 8.25 (d, $J_{H3\text{–}H4}$ 7.92, 2H, H_3), 8.11 (ddd, $J_{H4\text{–}H5}$ 7.59, 2H, H_4), 7.54 (ddd, 2H, H_5), 7.63 (m, 4H, $H_{2'}$), 7.15 (m, 6H, $H_{3'4'}$)
10. $Pd(CH_2SiMe_2Ph)_2(dpkt)$	0.16(s)	0.13(s)	8.57 (ddd, $J_{H6\text{–}H5}$ 5.28, $J_{H6\text{–}H4}$ 1.65, $J_{H6\text{–}H3}$ 0.66, 2H, H_6), 8.06 (ddd, $J_{H4\text{–}H3}$ 7.59, $J_{H4\text{-}H5}$ 7.91, 2H, H_4), 7.90–7.94 (m, 2H, H_3), 7.56 (ddd, $J_{H5\text{–}H3}$ 1.32, 2H, H_5), 7.61–7.65 (m, 4H, $H_{2'}$), 7.18–7.24 (m, 6H, $H_{3'4'}$)
11. $PdMe_2(bipy)$	1.11(s)		8.70 (m, $J_{H6\text{–}H5}$ 5.27, 2H, H_6), 6.87 (m, 2H, H3), 6.82 (m, 2H, H_4), 6.43 (ddd, $J_{H5\text{–}H4}$ 6.93, $J_{H5\text{–}H3}$ 1.64, 2H, H_5)
12. $Pd(CH_2CMe_2Ph)_2(dppe)$	2.48 (dd, J^{cis}6.6, J^{trans}11.9	1.23(s)	7.46 (m, 4H, $H_{2'}$), 7.02–7.06 (m, 6H, $H_{3',\ 4'}$), 7.58–7.65 (m, 8H, $H_{2,\ 6}$), 7.36–7.42 (m, 12H, $H_{3,\ 4,\ 5}$), 1.80–1.86 (m, 4H, CH_2P)

[a] In acetone-d_6, unless otherwise specified; δ/ppm relative to external TMS; J/Hz.

[b] In benzene-d_6.

Table 2
^{13}C- and ^{31}P-NMR characteristics of PdR_2L_2[a]

Compounds	$\underline{C}H_2Pd$	$Si\underline{C}H_3$	^{13}C[b] other: δ/ppm (assignment)	^{31}P[c] δ/ppm
1. $Pd(CH_2SiMe_3)_2$(cod)[d]	11.5	3.8	111.8 (CH), 29.0 (CH_2)	
2. $Pd[CH_2SiMe_2Ph]_2$(cod)	8.4	1.0	143.6 ($C_{1'}$), 133.0 ($C_{2'}$), 127.4 ($C_{4'}$), 126 ($C_{3'}$), 112.1 (CH), 28.2 (CH_2)	
3. $Pd(CH_2SiMe_3)_2$(bipy)	3.4	0.8	155.4 (C_2), 148.6 (C_6), 138.6 (C_3), 126.5 (C_4), 122.8 (C_5)	
4. $Pd(CH_2SiMe_3)_2$(phen)	0.2	3.4	156.8 (C_2), 148.6 (C_6), 143.3 (C_3), 137.7 (C_5), 127.4 (C_4), 125.5 (C_7)	
5. $Pd(CH_2SiMe_3)_2$(dpkt)	0.1	3.7	188.9 (C=O), 154.7 (C_2), 151.2 (C_6), 139.5 (C_3), 128.7 (C_4), 125.8 (C_5)	
6. $Pd(CH_2SiMe_3)_2$(dppp)	8.2[e]	4.6	135.7 (t, J_{P-C} 16.5, $C_{1'}$), 134.4 (t, J_{P-C} 5.5, $C_{2'6'}$),130.4 (s, $C_{4'}$), 128.8 (t, J_{P-C} 4.2, $C_{3',5'}$), 28.4 (t, J_{P-C} 11.6, CH_2P), 20.2 (t, J_{P-C} 4.2, CH_2)	6.4
7. *cis*-$Pd(CH_2SiMe_3)_2(PMe_3)_2$	9.8[f]	5.54	17.6 (t, J_{P-C} 24.75, PC)	-25.4
8. $Pd(CH_2SiMe_3)_2$(tmen) [d]	-6.7	4.8	58.8 (CH_2N), 47.8 (NCH_3)	
9. $Pd(CH_2SiMe_2Ph)_2$(bipy)	-0.4	2.1	155.3 (C_2), 148.6 (C_6), 138.5 (C_3), 126.4 (C_4), 122.6 (C_5), 145.8 ($C_{1'}$), 134.1 ($C_{2'}$), 127.8 ($C_{4'}$), 127.4 ($C_{3'}$)	
10. $Pd(CH_2SiMe_2Ph)_2$(dpkt)	-1.1	2.6	189.0 (C=O), 154.7 (C_2), 151.6 (C_6), 139.8 (C_3), 128.8 (C_4), 126.1 (C_5), 146.2 ($C_{1'}$), 134.7 ($C_{2'}$), 128.2 ($C_{3'}$), 128.5 ($C_{4'}$)	
11. $PdMe_2$(bipy)[d]	-6.6		155.6 (C_2), 148.2 (C_6), 138.6 (C_3), 126.8 (C_4), 122.9 (C_5)	
12. $Pd(CH_2CMe_2Ph)_2$(dppe)[d]	34.6[g]	37.9	136.3 (d, J_{P-C} 24.4, $C_{1'}$), 134.4 (d, J_{P-C} 12.2, $C_{2'}$), 129.2 (d, J_{P-C} 9.6, $C_{3'}$), 130.5 ($C_{4'}$), 25.0 (t, J_{P-C} 18.0)	29.4

[a] In acetone-d_6, unless otherwise specified; J/Hz.

[b] δ/ppm relative to external TMS.

[c] δ/ppm relative to external H_3PO_4.

[d] In benzene-d_6.

[e] dd, J^{trans}_{P-C} 104.3, J^{cis}_{P-C} 20.1.

[f] dd, J^{trans}_{P-C} 101.7, J^{cis}_{P-C} 15.1.

[g] dd, J^{trans}_{P-C} 102.5, J^{cis}_{P-C} 9.7.

was concentrated to ca. 5 ml and stored at ca. −30°C. The pure product was recovered by filtration as white crystals and was dried in vacuo. (Yield: 0.35 g, 80%). Analyses: found (calc.): %C, 49.1 (49.4); %H, 8.8 (8.8).

IR (cm^{-1}): 2958s, 2964vs, 2907vs, 2885sh, 1466m, 1451m, 1429s, 1251s, 1239vs, 843vs, 824vs, 675s, 512w.

*3.3. Preparation of bis(dimethylphenylsilylmethyl)-(cycloocta-1,5-diene)palladium(II) (**2**)*

This compound was prepared by a procedure exactly analogous to that of **1** (above), from $PdCl_2$(cod) (0.29 g, 1 mmol) in diethyl ether (30 ml) and $Mg(SiCH_2Me_2Ph)Cl$ (6 ml, 0.40 M solution, 2.4 mmol). After the reaction, a degassed solution of acetone (ca. 1 ml) and hexane (ca. 20 ml) was added to the reaction mixture at −78°C and the mixture was allowed to warm to about −10°C. The volatiles were removed in vacuo. The residue was treated with hexane, the resulting solution was cold filtered and diethyl ether added to induce crystallisation. The pure product was obtained as pale needles. (Yield: 0.46 g, 90%). Analyses: found (calc.): %C, 60.8 (60.9); %H, 7.5 (7.5). IR (cm^{-1}): 3063m, 2974vs, 2882vs, 1588vw, 1565w, 1482m, 1462s, 1240vs, 1109vs, 823vs, 736vs, 518m.

*3.4. Preparation of bis(trimethylsilylmethyl)-(2,2′-bipyridyl)palladium(II) (**3**)*

A solution of 2,2′-bipyridyl (0.076 g, 0.5 mmol) in diethyl ether (10 ml) was added slowly to a stirred solution of $Pd(CH_2SiMe_3)_2$(cod) (0.195 g, 0.5 mmol) in the same solvent (10 ml) at −5°C. The mixture was stirred at ambient temperature for 5 min. The volatiles were removed in vacuo. Pure yellow crystalline product was obtained by recrystallization from an acetone–hexane mixture (yield: 0.20 g, 92%). Analyses; found (calc.): %C, 49.3 (49.5); %H, 6.9 (6.9); %N, 6.4(6.4). IR (cm^{-1}): 2963vs, 2959sh, 2861s, 1595w, 1564vw, 1468m, 1234m, 834m, 831m, 818m, 757m, 531w.

*3.5. Preparation of bis(trimethylsilylmethyl)-(1,10-phenanthroline)palladium(II) (**4**)*

This complex was prepared by a procedure exactly analogous to that of **3** (above), from a 1:1 admixture of 1,10-phenanthroline and $Pd(CH_2SiMe_3)_2$(cod) in diethyl ether. A yellow crystalline product was obtained from acetone hexane in quantitative yield. Analyses; found (calc.): %C, 52.3 (52.1); %H, 6.6 (6.6); %N, 5.8 (6.1). IR (cm^{-1}): 2938vs, 2898s, 2859m, 1625w, 1511m, 1467m, 1435s, 1250sh, 1235s, 840vs, 724s, 530w.

*3.6. Preparation of bis(trimethylsilylmethyl)-[di(2-pyridyl)ketone]palladium(II) (**5**)*

This derivative was synthesized by a procedure exactly analogous to that of **3** (above), from an equimolar conjunction of di(2-pyridyl)ketone and $Pd(CH_2SiMe_3)_2$-(cod) in diethyl ether. Pure orange crystalline **5** was recovered after recrystallization from hexane (yield: 95%). Analyses; found (calc.): C, 49.2 (49.1); H, 6.6 (6.5); N, 6.0 (6.0); IR (cm^{-1}): 2957vs, 2909s, 2844s, 1690m, 1589w 1466m, 1238m, 846m, 817m, 754m, 527w.

*3.7. Preparation of bis(trimethylsilylmethyl)-[bis-1,3-(diphenylphosphino)propane]palladium(II) (**6**)*

This complex was synthesized by a procedure exactly analogous to that of **3** (above), from dppp and (cod)$Pd(CH_2SiMe_3)_2$. The product was obtained as colourless needles after recrystallization from an ether–hexane mixture (Yield: 88%). Analyses; found (calc.): %C, 60.7 (61.0); %H, 7.0 (6.4). IR (cm^{-1}): 3073w, 2962vs, 2901vs, 2892s, 1587vw, 1482m, 1467m, 1437m, 1263m, 1098m, 845m, 818m, 742m, 695s, 509s, 483m.

3.8. Preparation of cis*-bis(trimethylsilylmethyl)bis-(trimethylphosphine)palladium(II) (**7**)*

Excess PMe_3 (ca. 3-fold) was added via syringe to a stirred solution of $Pd(CH_2SiMe_3)_2$(cod) (0.25 g, 0.64 mmol) in diethyl ether (5 ml) at −10°C. The mixture was allowed to warm to ambient temperature and the volatiles were removed in vacuo. Compound **7** was obtained as a white gummy solid (yield: 100%). Analyses; found (calc.): %C, 38.9 (38.8); %H, 9.3 (9.3). IR (cm^{-1}): 2950vs, 2878vs, 1462vs, 1270s, 1237vs, 823s, 674s, 520w.

*3.9. Preparation of bis(trimethylsilylmethyl)(tetramethylethylenediamine)palladium(II) (**8**)*

Excess *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (ca. 2-fold) was added via syringe to a solution of $Pd(CH_2SiMe_3)_2$(cod) (0.20 g, 0.51 mmol) in diethyl ether (8 ml) under argon at −78°C. The mixture was stored at ca. −30°C overnight, volatiles were removed in vacuo, below −5°C. The pure compound was obtained as white needles, after recrystallization of the residue from *n*-hexane (yield: 0.12 g, 60%). Analyses; found (calc.): %C, 42.3 (42.4); %H, 9.9 (9.7); %N, 7.0 (7.1). IR (cm^{-1}): 2945vs, 2868vs, 2833s, 2788m, 1616w, 1460vs, 1274sh, 1236vs, 845vs, 823vs, 795s, 673s, 523w.

*3.10. Preparation of bis(dimethylphenylsilylmethyl)-(2,2′-bipyridyl)palladium(II) (**9**)*

This complex was synthesized by a procedure exactly analogous to that of **3** (above), from equimolar admixture of 2,2′-bipyridyl and $Pd(CH_2SiMe_2Ph)_2(cod)$ in diethyl ether. The product was obtained as yellow crystals (yield: 95%). Analases; found (calc.): %C, 60.0 (59.9); %H, 6.1 (6.1); %N, 5.0 (5.0). IR (cm^{-1}): 3078m, 2949vs, 2853vs, 1597m, 1584w, 1468s, 1441s, 1236s, 1106s, 835s, 804s, 756vs, 552w, 540.

*3.11. Preparation of bis(dimethylphenylsilylmethyl)[di(2-pyridyl)ketone]-palladium(II) (**10**)*

This derivative was synthesized by a procedure exactly analogous to that of **3** (above), from addition of di(2-pyridyl)ketone to equimolar $Pd(CH_2SiMe_2Ph)_2$-(cod) in diethyl ether. The product was obtained as a gummy orange semi-solid in essentially quantitative yield. Analyses; found (calc.): %C, 59.2 (59.1); %H, 5.8 (5.8); %N, 4.8 (4.7). IR (cm^{-1}): 3064s, 2947vs, 2892s, 2854s, 1683vs, 1590s, 1425s, 1307s, 1238s, 1105s, 804vs, 537w.

*3.12. Preparation of dimethyl(2,2′-bipyridyl)-palladium(II) (**11**)*

The compound MgMeCl in THF (2.5 ml, 1.0 M, 2.5 mmol) was added to a suspension of $PdCl_2(cod)$ (0.29 g, 1 mmol) diethyl ether (30 ml) at −78°C. The mixture was allowed to warm to about −10°C, and stirred at this temperature for 30 min. After cooling the mixture to −78°C, a prepared mixture of acetone (1 ml) and hexane (10 ml) was added slowly, followed by a solution of 2,2′-bipyridyl (0.16 g, 1 mmol) in diethyl ether (10 ml). The mixture was allowed to warm to ambient temperature. After stirring for 20 min, the solution was filtered. The filtrate was evaporated to dryness in vacuo. Pure product was obtained as yellow crystals after recrystallization of the residue from an acetone–hexane mixture (yield: 0.25 g, 86%). Analyses; found (calc.): %C, 49.0 (49.2); %H, 4.6 (4.8); %N, 9.5 (9.6). IR (cm^{-1}): 3073vw, 2922vs, 2850s, 1599s, 1467s, 1442vs, 1311m, 1157m, 752vs, 730vs, 530vw, 524w.

*3.13. Preparation of dineophyl)[bis-1,3-(diphenylphosphino)propane]palladium(II) (**12**)*

This complex was synthesized by a procedure exactly analogous to that of **11** (above), using appropriate molar quantities of $PdCl_2(cod)$, $Mg(CH_2CMe_2Ph)Cl$ and dppe. The product was obtained as a pale solid after recrystallization from acetone (yield: 80%). Analyses; found (calc.): %C, 66.5 (66.8); %H, 7.0 (7.2). IR (cm^{-1}): 3071w, 2956sh, 2944vs, 2851s, 1586w, 1482m, 1468m, 1434s, 1228m, 1093m, 740s, 692vs, 529s.

4. Conclusions

With careful manipulation, bis(silylmethyl)palladium(II) complexes with η-diene ligands—$Pd(CH_2SiMe_3)_2(cod)$ and $Pd(CH_2SiMe_2Ph)_2(cod)$—may be isolated in good yields. Via diene-displacement, these are convenient precursors to a related series of dialkylpalladium derivatives with N- and P-donor ancillary ligands. Isolation of the η-diene–metal intermediate is not always necessary for success, however, and $PdMe_2(bipy)$ and $Pd(CH_2CMe_2Ph)_2(dppe)$ have been prepared in excellent yields (> 80%) in this way (Scheme 1).

Acknowledgements

We are most grateful to the British Council and to the EPSRC for successive awards of Postdoctoral Fellowships (to P. Yi) and to the Nuffield Foundation for the award of a Research Fellowship (to G.B. Young) in the course of this work. We additionally thank Johnson-Matthey for their continued support by way of generous loans of palladium precursors. Thanks are also due to Dick Sheppard and Paul Hammerton for invaluable assistance with high-field NMR measurements.

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