Journal of Organometallic Chemistry, 240 (1982) 95–102
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

REACTIONS OF A CHELATED ALKYLPALLADIUM COMPOUND

E.L. WEINBERG, B.K. HUNTER and M.C. BAIRD *

Department of Chemistry, Queen's University, Kingston, K7L 3N6 (Canada)

(Received May 4th, 1982)

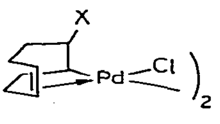
Summary

The chemistry of the compound $[\overline{Pd(CH_2CHRCH_2N}Me_2)Cl]_2$ (V, R = $CH(CO_2Et)_2$) with nucleophilic (PPh_3, pyridine, CO) and electrophilic (H_2, HCl) reagents is studied. Although the nucleophiles cleave the chloride bridges, they do not readily disrupt the Pd–N bond, and both V and its adducts are very stable with respect to decomposition via olefin elimination. As expected, however, H_2 and HCl cleave the Pd–C bond to give $CH_3CHRCH_2NMe_2$ and either Pd metal or a palladium chloride complex, respectively.

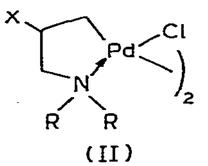
Introduction

Organopalladium compounds are currently of great interest because of their roles in a wide variety of catalytic processes [1,2], but surprisingly little is known about the properties of simple, σ-bonded alkylpalladium compounds. Although readily prepared by, for instance, oxidative addition of alkyl halides to palladium(0) compounds [3] or alkylation/arylation of olefin–palladium(II) complexes [4,5], compounds with β-hydrogen atoms are usually exceedingly labile and readily eliminate olefin [3–5].

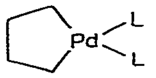
When a second potential donor atom is present in the alkyl ligand, however, relatively stable chelate complexes can be isolated; examples are I [6], II [7,8], III [9] and IV [10]. Chelation apparently prevents the β-hydrogen atom(s) from assuming the stereochemical positioning necessary for β-hydrogen migration to occur [11,12].



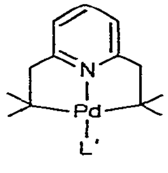
(I)



(II)



(III)



(IV)

(R = alkyl ; X = R, OR, OH ; L = tertiary phosphine ; L' = nitrogen donor)

0022-328X/82/0000-0000/$02.75

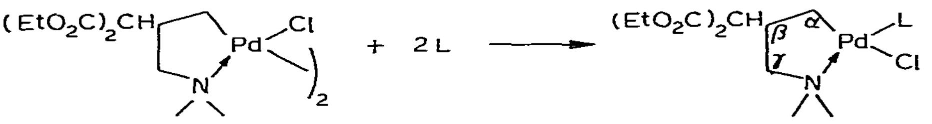
Compounds of types I–IV thus present interesting opportunities to study alkylpalladium chemistry, both of the chelates and, if the chelate interaction can be disrupted, of the monodentate alkyl species. We have begun such a study, utilizing in the first instance V, of type II.

Compounds of type II were first prepared over a decade ago by Cope et al. [7], and were briefly investigated by Holton [8,13,14] a few years ago as intermediates in a number of synthetically useful reactions. Compound V has been briefly discussed in the literature [8,14], although its chemistry has been little studied.

Results and discussion

Reactions with nucleophilic reagents (triphenylphosphine, pyridine, diphos and carbon monoxide)

Consistent with results published for similar systems [15–18], we find that V reacts with triphenylphosphine and pyridine as in eq. 1.



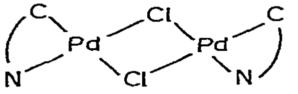
(1)

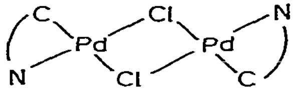
(V)

(VI, L = PPh_3;
VII, L = py)

The suggested formulations of VI and VII are consistent with the ^1H NMR spectra, which are quite complicated. Since the β-carbon atom of the chelating alkyl ligand is chiral, then the α- and γ-methylene hydrogen atoms, the *N*-methyl groups, the two ester groups and each pair of methylene hydrogen atoms within each ester moiety all constitute pairs of diastereotopic atoms or groups. Thus doubling of all these resonances in the spectrum might be expected. Furthermore, space-filling molecular models strongly suggest that the malonate group will prefer a quasi-equatorial position on the five-membered ring, thereby forcing the α- and γ-methylene hydrogens and the *N*-methyl groups likewise into quasi-axial and -equatorial positions, and likely increasing the intrinsic diastereotopicity of each pair of resonances.

While predictions of the chemical shift differences cannot be made a priori, the pertinent resonances of compounds V–VII do generally show the expected doubling (see Experimental Section). In addition, for V, further doubling is also resolved for some resonances (α-CH_2, malonate methine), and may be interpreted either in terms of the diastereomeric nature of the dimer, or as indicating the presence of geometrical isomers, i.e.:

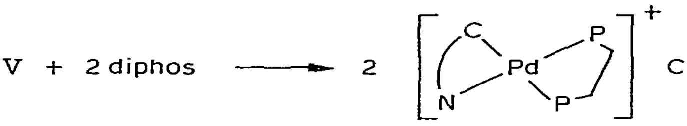




The ^{31}P NMR spectrum of VI exhibits only a single resonance, clearly establishing that, for this compound only one geometrical isomer is present. In addition, the ν(Pd–Cl) values for VI and VII (273 and 276 cm^{-1}, respectively) are characteristic of chlorine *trans* to carbon (260–300 cm^{-1}) rather than to a tertiary amine (320–355 cm^{-1}) [17–19].

Although the palladium–nitrogen bond of some *ortho*-palladated complexes can be broken by triphenylposphine [20,21], addition of triphenylphosphine to a solution of VI does not cause fission of the Pd–N bond as the ^{31}P NMR signals of both VI and uncoordinated PPh_3 are observed. However, disappearance of the phosphorus coupling to the *N*-methyl protons (^{1}H NMR at 60 MHz, 298 K) indicates exchange of free and coordinated phosphine. Likewise, the Pd–N bond of the pyridine complex VII is not broken by excess pyridine.

Addition of two moles diphos ($Ph_2PCH_2CH_2PPh_2$) to V proceeds as in eq. 2 to give the cationic chelate complex VIII, a 1/1 electrolyte in acetonitrile. The

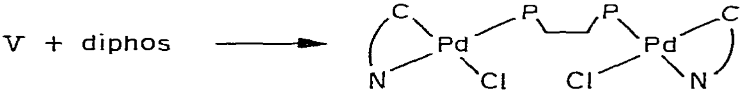


(2)

(VIII)

chelating nature of the diphos ligand is clearly evident from the ^{31}P NMR spectrum, in which two mutually coupled phosphorus resonances at δ 56.2 and 37.3 ppm (^3J(PP) 24 Hz) are observed. These are assigned on the basis of relative *trans* influences [23,24] to the phosphorus atoms *trans* to nitrogen and *trans* to carbon, respectively (see below).

In contrast, addition of an equimolar amount of diphos to V yields the bridging diphos complex IX eq. 3). The phosphorus NMR spectrum of IX shows two



(3)

(IX)

phosphorus resonances at ~ δ 35.0 ppm, separated by less that 0.05 ppm, but no phosphorus–phosphorus coupling. If the distinct phosphorus signals arise from the P atoms being in different chemical environments in the same complex (i.e., one P *trans* to C, one P *trans* to N) then phosphorus–phosphorus coupling would be readily observed. Therefore, both phosphorus atoms must be *trans* to the same type of atom (i.e., both *trans* to N or both *trans* to C). Furthermore, if the two phosphorus signals are the result of a 1/1 mixture of these types of geometrical isomers of IX, then the chemical shift difference between them, Δδ, would almost certainly be greater than 0.05 ppm (cf. VIII, for which Δδ 19 ppm). The best explanation for the nonequivalence of the phosphorus atoms of IX would therefore appear to be the fact that both chelated alkyl groups of IX contain chiral carbon atoms, leading to the formation of diastereomers which exhibit slightly different phosphorus chemical shifts. Since the far infrared spectrum of IX is complicated by absorptions due to diphos, assignment of the ν(Pd–Cl) value (274 cm^{-1}) is only tentative. However, the high *trans* influences of both alkyl groups and tertiary phosphines [1,22] suggest the stereochemistry proposed, that is both chlorines *trans* to carbon. Returning to the ^{31}P NMR spectrum of VIII, we note that the resonance at δ 56.2 ppm is much further downfield than that in the bridging diphos complex IX (Δδ 21 ppm). This is consistent with the general observation that in five-membered phosphorus chelate complexes, the "ring contribution" results in a deshielding of the phosphorus resonance by 21–33 ppm relative to similar monodentate species [24,25].

When carbon monoxide is bubbled through a solution of V in $CDCl_3$, the colour fades within a few minutes. While the ^1H NMR spectrum suggests that a single new species has been formed, the IR spectrum exhibits a new terminal carbonyl stretching band at 2120 cm^{-1}. Although the carbonyl complex cannot be isolated pure (bubbling nitrogen through the solution regenerates V), the species in solution, X, is undoubtedly analogous to VI and VII ($L = CO$) [26]. Interestingly, although monodentate σ-alkylpalladium complexes readily undergo CO insertion to give acyl species [1], X gave no indication for the formation of such a compound. Even attempts to trap small equilibrium amounts of an acyl species by warming in methanol, a solvent which is known to react with acylpalladium complexes to give esters [27], failed.

The reluctance of X to undergo insertion is unusual, although not unprecedented for some chelated alkylpalladium complexes [9,26]. However, it has been reported that a complex of type II ($X = OMe$) does undergo carbonylation in ethanol to give the corresponding ethyl ester [28], and thus the diethylmalonate group appears to exhibit a rather unusual deactivating effect.

Attempts to react V with styrene were fruitless, no reaction being apparent after 24 h at 80°C. Insertion reactions with methyl vinyl ketone have been reported [8,13].

Reactions with electrophilic reagents (hydrogen, hydrogen chloride, methyl iodide)

Holton and Kjonaas [8,14] have reported that V can be reduced by hydrogen to the corresponding γ-aminodiester XI (eq. 4).

$$\mathrm{V} + 2H_2 \rightarrow \underset{\text{(XI)}}{2Me_2NCH_2CHMeCH(CO_2Et)_2} + 2Pd + 2HCl \qquad (4)$$

In our hands, however, a $CDCl_3$ solution of V reacted with hydrogen to yield palladium metal and a colourless organic product (XII) whose ^1H NMR spectrum shows the presence of a protonated amine (δ(NH) 12.0 ppm (br); δ(NMe) 2.88 ppm, d $^3J(HNCH_3)$ 5 Hz). The protonated product, which is the conjugate acid of XI, can be deprotonated with sodium bicarbonate to yield a colourless solid (XI) whose ^1H NMR spectrum is consistent with that of the product reported previously.

Reaction of V with anhydrous hydrogen chloride yielded a red, hygroscopic solid (XIII) which could not be obtained pure, but whose ^1H NMR spectrum again showed the presence of a protonated amine. While the spectra of XII and XIII were not identical, presumably because of the presence of different anions, treatment of the latter with first triphenylphosphine then sodium bicarbonate gave *trans*-$PdCl_2(PPh_3)_2$ [29] and XI.

While no intermediates could be detected during the hydrogen and hydrogen chloride cleavage reactions, it seems likely that they proceed via an oxidative addition–reductive elimination process [30]. Attempts to react V with methyl iodide yielded a complex mixture of products which could not be satisfactorily identified. However, significant amounts of methyl chloride were found, consistent with reductive elimination from a methylpalladium(IV) intermediate, and a transient intermediate with a methyl resonance at δ 2.20 ($CDCl_3$) ppm is tentatively suggested to be a methylpalladium(IV) species [31].

Experimental

NMR spectra were obtained on Bruker HX60 and CXP200 spectrometers: unless otherwise stated, all spectra were run in $CDCl_3$. ^1H at 200 MHz, ^{13}C at 50.3 MHz, ^{31}P at 80.9 MHz. IR spectra were run on Beckman 4240 and Perkin–Elmer 180 spectrometers, conductivity measurements were carried out on a Philips PR9501 conductivity meter, and melting points (uncorrected) were done on Gallenkamp Melting Point Apparatus. Chemical Analyses were performed by Canadian Microanalytical Services Ltd., Vancouver, B.C.

Compound V was prepared by the method of Holton and Kjonaas [8,14]. M.p. 160–161°C (decomp.). Lit. 184–187°C (decomp.). ν(CO) 1678–1775 cm^{-1}($CDCl_3$). ν(PdCl) 326,279 cm^{-1} (Nujol). ^1H NMR: δ 1.25 (t, J 7 Hz, malonate CH_3), 1.8, 2.1 (2br resonances, α-CH_2), 2.4–2.6 (br, γ-CH_2), 2.6 (found via double resonance experiments, β-CH), 2.67, 2.80 (2 singlets, NCH_3), 3.17 (d, J 8 Hz, malonate CH), 4.16 (m, malonate CH_2) ppm. ^{13}C NMR: δ 14.1 (malonate CH_3), 24.0, 25.8 (α-C), 41.5 (β-C), 49.7, 53.8 (NCH_3), 52.9 (malonate CH), 61.4, 61.5 (malonate CH_2), 70.6 (γ-C), 167.7, 167.9 (CO_2) ppm.

Reaction of V with pyridine. 0.2 ml (240 mmol) pyridine was added to 0.41 g (52 mmol) V in 5 ml $CHCl_3$. The mixture was stirred for 10 min under nitrogen, the colour changing from bright to pale yellow. The solvent was then removed under reduced pressure, the residue was taken up in 1/10 chloroform/toluene, and ethyl ether was added to give white crystals of VII. Found: C, 43.71; H, 5.69; N, 5.90. $C_{17}H_{27}ClN_2O_4Pd$ calcd.: C, 43.88; H, 5.85; N, 6.02%. M.p. 131–132°C (decomp.); ν(PdCl) 276 cm^{-1} (Nujol). ^1H NMR: δ 1.23, 1.27 (2 triplets, J 7 Hz, malonate CH_3, 1.78 (d, J 8 Hz, α-CH_2), 2.5–2.8 (m, β-CH, γ-CH_2), 2.86, 2.92 (2 singlets, NCH_3), 3.20(d, J 8 Hz, malonate CH), 4.17, 4.19, 4.20 (3 quartets, latter two of intensity half that of the first, J 7 Hz, malonate CH_2), 7.2, 7.7, 8.7 (multiplets, pyridine) ppm. ^{13}C NMR: δ 14.1 (malonate CH_3), 28.5 (α-C), 41.3 (β-C), 49.5, 54.0 (NCH_3), 54.0 (malonate CH), 61.4, 61.5 (malonate CH_2), 71.6 (γ-C), 168.0, 168.1 (CO_2), 124.8, 137.3, 152.9 (pyridine) ppm.

Reaction of V with triphenylphosphine. 0.16 g (60 mmol) PPh_3 in 4 ml CH_2Cl_2 was added to 0.23 g (30 mmol) V in 10 ml CH_2Cl_2. The reaction mixture was stirred for 10 min, the colour fading to light yellow. The solvent was removed under reduced pressure, the yellow residue was dissolved in toluene, and yellow crystals of VI were precipitated on the addition of 1/1 ethyl ether/petroleum ether (b.p. 30–60°C). Found: C, 55.84; H, 5.35; N, 2.10; Cl, 5.79. $C_{30}H_{38}ClNO_4PPd$ calcd.: C, 55.57; H, 5.75; N, 2.16; Cl, 5.47%. M.p. 160–161°C (decomp.); ν(PdCl) 273 cm^{-1} (Nujol). ^1H NMR: δ 0.93, 1.2 (2 multiplets, α-CH_2), 1.06, 1.20 (2 triplets, J 7 Hz, malonate CH_3), 2.4–2.7 (m, γ-CH_2), 2.8 (found via double resonance experiments, β-CH), 2.86 (s, br, NCH_3), 2.99 (d, J 10 Hz, malonate CH), 3.85, 3.87, 4.11, 4.12 (4 quartets, J 7 Hz, malonate CH_2), 7.3–7.8 (m,Ph) ppm. ^{13}C NMR: δ 14.1, 14.2 (malonate CH_3), 33.2 (α-C), 42.0 (β-C), 47.8, 52.1 (NCH_3), 55.3 (malonate CH), 61.2, 61.4 (malonate CH_2), 69.7 (γ-C), 126–137 (m,Ph), 167.8, 168.2 (CO_2) ppm. ^{31}P NMR: δ 36.5 ppm.

Reactions of V with diphos. (a) 0.16 g (39 mmol) diphos in 5 ml $CHCl_3$ was added to 0.30 g (39 mmol) V in 10 ml $CHCl_3$, and the reaction mixture was stirred 10 min under nitrogen to give a pale yellow solution. The solvent was removed under reduced pressure, and the residue was recrystallized from toluene/ethyl ether to give off-white crystals of IX. Found: C, 52.01; H, 5.57; N, 2.37; Cl, 6.44. $C_{50}H_{68}N_2O_8P_2Pd_2$ calcd.: C, 51.29; H, 5.85; N, 2.39; Cl, 6.00%. M.p. 165–166°C (decomp); ν(PdCl) 274 cm^{-1} (Nujol). ^{1}H NMR: δ 1.0 (found via double resonance experiments, α-CH_2), 1.00, 1.01, 1.17 (3 triplets, last with double the intensity of each of the others, *J* 7 Hz, malonate CH_3), 2.36–2.60 (m, β-CH, γ-CH_2, PCH_2), 2.74, 2.77 (br singlets, NCH_3), 2.96 (d, *J* 10 Hz, malonate CH), 3.86, 4.08, 4.09 (4 quartets, first with double the intensity of each of the others, *J* 7 Hz, malonate CH_2), 7.5 (m,Ph) ppm. ^{13}C NMR: δ 13.9, 14.0 (malonate CH_3), 24.2 (d, *J*(PC) 13 Hz, PCH_2), 31.4 (d, *J*(PC) 7.5 Hz, α-C), 41.6 (β-C), 47.4, 51.6 (NCH_3), 55.0 (malonate CH), 61.1, 61.2 (malonate CH_2), 68.9 (γ-C), 125–135 (m,Ph), 167.8, 168.1 (CO_2) ppm. ^{31}P NMR: δ 35.0 (d) ppm.

(b) 0.24 g (60 mmol) diphos in 10 ml $CHCl_3$ was added to 0.23 g (60 mmol) V in 20 ml $CHCl_3$, and the reaction mixture was stored 10 min under nitrogen to give a light orange solution. The solvent was removed at reduced pressure, the residue was taken up in 1/10 $CHCl_3/C_6H_6$, and white crystals of VIII were precipitated with ethyl ether. Found: C, 57.32; H, 5.99; N, 1.77. $C_{38}H_{46}ClNO_4P_2Pd$ calcd.: C, 58.17; H, 5.91; N, 1.79%. M.p. 128–129°C (decomp.). Conductivity: Λ_M 155 ohm^{-1} cm^2 mol^{-1} (10^{-3} *M* in MeCN at 25°C) consistent with formulation as a 1/1 electrolyte [34]. ^{1}H NMR: δ 1.05, 1.18 (2 triplets, *J* 7 Hz, malonate CH_3), 1.2, 1.7 (found via double resonance experiments, α-CH), 2.40, 2.63 (2 br singlets, NCH_3), 2.1–2.9 (m, β-CH, γ-CH_2, PCH_2), 3.19 (d, *J* 8 Hz, malonate CH), 3.98, 4.11 (2 quartets, *J* 7 Hz, malonate CH_2), 7.5 (m, Ph) ppm. ^{13}C NMR: δ 14.0 (malonate CH_3), δ 27.4 (q, *J*(PC) 20.32 Hz, PCH_2), 28.9 (q, *J*(PC) 11.28 Hz, PCH_2), 39.0 (d, *J*(PC) 82 Hz, α-C), 42.2 (β-C), 55.3, 55.5(NCH_3), 61.4, 61.6 (malonate CH_2), 70.8(γ-C), 125–135 (m, Ph), 167.9, 168.2 (CO_2) ppm; malonate CH obscured. ^{31}P NMR: δ 37.7, 56.2 (AX pattern, *J*(PP) 24 Hz) ppm.

Reaction of V carbon monoxide. Carbon monoxide was bubbled through a solution of V in $CDCl_3$ for 10 min, giving a colourless solution. The IR spectrum of the solution exhibited a strong ν(CO) at 2120 cm^{-1}, while the ^{1}H NMR spectrum was consistent with there being only one product, presumably X. ^{1}H NMR: δ 1.28, 1.29 (2 triplets, *J* 7 Hz, malonate CH_3), 1.85 (dd, *J* 9, 12 Hz, one α-CH_2 proton) 2.4–3.0 (m, β-CH, γ-CH_2, other α-CH_2 proton), 2.78, 2.80 (2 singlets, NCH_3), 3.31 (d, *J* 8 Hz, malonate CH), 4.21, 4.22, 4.24 ppm (2 quartets, last with intensity double that of each of the others, malonate CH_2).

Under an atmosphere of carbon monoxide, a solution of X is stable for at least 12 h. On removing the solvent under reduced pressure, or on bubbling nitrogen through a solution at room temperature, substantial reversion to V occurs.

Reaction of V with styrene. A 4/1 mixture of styrene and V in C_6D_6 was sealed in an NMR tube and heated at 80°C for 24 h. No reaction took place, as judged by the NMR spectrum.

Reaction of V with hydrogen. Hydrogen gas was bubbled into a solution of V in $CDCl_3$, giving a colourless solution and a precipitate of palladium metal. The ^{1}H NMR spectrum showed the presence of only one product, XII: δ 1.29 (two triplets, *J* 7 Hz, malonate CH_3), 1.41 (d, *J* 7 Hz, α-CH_3), 2.66(m, β-CH), 2.6–3.2(m, γ-CH_2, 2.84(s, NCH_3), 3.46(d, *J* 6 Hz, malonate CH), 4.26(m, malonate CH_2) ppm. If the solution is rigourously dry, a broad singlet at δ 12.0 ppm, attributable to NH, can also be observed.

Stirring the above solution with sodium bicarbonate for several hours resulted in deprotonation to give XI. ^1H NMR: δ 1.02(d, J 6 Hz, α-CH_3), 1.27(double triplet, J 7 Hz, malonate CH_3), 2.0–2.5(m, β-CH, γ-CH_2), 2.23(s, NCH_3), 3.38(d, J 6 Hz, malonate CH), 4.16, 4.21 ppm (2 quartets, J 7 Hz, malonate CH_2).

The deprotonation reaction could be reversed by bubbling anhyd. HCl through the solution for 5 min.

Reaction of V with anhydrous HCl. Anhydrous HCl was bubbled through a solution of V in $CHCl_3$, causing the colour to change from yellow to red. The solvent was removed under reduced pressure and the red residue was dissolved in $CDCl_3$. The ^1H and ^{13}C NMR spectra suggested the presence of a single product. ^1H NMR: δ 1.32 (2 triplets, J 7 Hz, malonate CH_3), 1.39 (d, J 6 Hz, α-CH_3), 2.7(m, β-CH), 3.2–3.4(m, γ-CH_2), 3.13, 3.27 (2 doublets, J 5 Hz, NCH_3), 3.54(d, J 6 Hz, malonate CH), 4.27, 4.28(2 quartets, J 7 Hz, malonate CH_2) 8.0(br, NH) ppm. ^{13}C NMR: δ 14.2 (malonate CH_3), 17.4(α-C; a quartet in the coupled spectrum); 29.6(β-C), 44.2, 46.8(NCH_3), 55.5(malonate CH), 62.4(malonate CH_2), 62.5(γ-C), 168.1, 168.3(CO_2) ppm.

Addition of excess triphenylphosphine yielded yellow crystals of *trans*-$PdCl_2(PPh_3)_2$, identified by spectral comparisons with an authentic sample [29]. Treatment of the resulting solution with sodium bicarbonate gave a product identical (^1H NMR, GLC, TLC) with XI.

Reaction of V with methyl iodide. Reactions of V with methyl iodide (10-20 × excess) in C_6D_6 and $CDCl_3$ were studied in sealed NMR tubes. Although no reactions were apparent at room temperature, a complex series of spectral changes was observed at 80°C over 30 h. Initially, a new singlet appeared (δ 2.20 in $CDCl_3$, 1.49 ppm in C_6D_6), slightly downfield from the resonance in methyl iodide. The new singlet first grew, then decreased in intensity as a resonance attributable to methyl chloride (δ 3.02 in $CDCl_3$, 2.32 ppm in C_6D_6) appeared. The spectra became very complicated, indicating the presence of a variety of products, and the reactions were abandoned.

Acknowledgements

Financial support by the Natural Sciences and Engineering Research Council of Canada (grant to M.C.B., scholarship to E.L.W.) and Queen's University is gratefully acknowledged. We also thank Johnson Matthey, Ltd., for a loan of palladium chloride.

References

1 P.M. Maitlis, The Organic Chemistry of Palladium, Vols. 1 and 2, Academic Press, New York, 1971.
2 B.M. Trost, Tetrahedron, 33 (1977) 2615.
3 J.K. Stille and K.S.Y. Lau, J. Amer. Chem. Soc., 98 (1976) 5841.
4 T. Hayashi and L.S. Hegedus, J. Amer. Chem. Soc., 99 (1977) 7093.
5 R.F. Heck, Pure Appl. Chem., 50 (1978) 691.
6 J. Chatt, L.M. Vallarino and L.M. Venanzi, J. Chem. Soc., (1957) 3413.
7 A.C. Cope, J.M. Kliegman and E.C. Friedrich, J. Amer. Chem. Soc., 89 (1967) 287.
8 R.A. Holton and R.A. Kjonaas, J. Amer. Chem. Soc., 99 (1977) 4177.
9 P. Diversi, G. Ingrosso, A. Lucherini and S. Murtas, J. Chem. Soc. Dalton Trans, (1980) 1633.
10 G.R. Newkome, T. Kawato, D.K. Kohli, W.E. Puckett, B.D. Olivier, G. Chiari, F.R. Fronczek and W.A. Deutsch, J. Amer. Chem. Soc., 103 (1981) 3423.
11 D.L. Thorn and R. Hoffmann, J. Amer. Chem. Soc., 100 (1978) 2079.

12 J.X. McDermott, J.F. White and G.M. Whitesides, J. Amer. Chem. Soc., 98 (1976) 6521.
13 R.A. Holton and R.A. Kjonaas, J. Organometal. Chem., 133 (1977) C5.
14 R.A. Holton and R.A. Kjonaas, J. Organometal. Chem., 142 (1977) C15.
15 M.I. Bruce, Angew. Chem. Int. Ed. Engl., 16 (1977) 73.
16 B. Crociani, P. Uguagliati, T. Boschi and U. Belluco, J. Chem. Soc. A, (1968) 2869.
17 B. Crociani, T. Boschi, R. Pietropaolo and U. Belluco, J. Chem. Soc. A, (1970) 531.
18 J. Dehand, M. Pfeffer and M. Zinsius, Inorg. Chim. Acta, 13 (1975) 299.
19 P. Braunstein, J. Dehand and M. Pfeffer, Inorg. Nucl. Chem. Lett., 10 (1974) 581.
20 A.G. Constable, W.S. McDonald, L.C. Sawkins and B.L. Shaw, J. Chem. Soc. Dalton, (1980) 1992.
21 A.G. Constable, W.S. McDonald and B.L. Shaw, J. Chem. Soc. Dalton, (1980) 2282.
22 P. Braunstein, D. Matt, Y. Dusausoy, J. Fischer, A. Mitschler and L. Ricard, J. Amer. Chem. Soc., 103 (1981) 5115.
23 D.A. Slack, I. Greveling and M.C. Baird, Inorg. Chem. 18 (1979) 3125.
24 P.S. Pregosin and R.W. Kung, NMR Basic Principles and Progress, Vol. 16, Springer-Verlag, New York, 1979.
25 P.E. Garrou, Chem. Rev., 81 (1981) 229.
26 H. Onoue, K. Nakagawa and I. Moritani, J. Organometal. Chem., 35 (1972) 217.
27 J.K. Stille, L.F. Hines, R.W. Fries, P.K. Wong, D.E. James and K.S.Y. Lau, Adv. Chem. Ser., No. 132 (1974) 90.
28 D. Medema, R. van Helden and C.F. Kohll, Inorg. Chim. Acta, 3 (1969) 255.
29 F.R. Hartley, The Chemistry of Platinum and Palladium, Applied Science Publishers, Ltd., London, 1973.
30 J.K. Kochi, Organometallic Mechanisms and Catalysis, Academic Press, New York, 1978, Chap. 12.
31 The species resonates at δ 1.49 ppm in C_6D_6. These chemical shifts compare well with those of methylplatinum(IV) species [32].
32 J.D. Ruddick and B.L. Shaw, J. Chem. Soc. A, (1969) 2801, 2964.
33 P.J. Davidson, M.F. Lappert and R. Pearce, Chem. Rev., 76 (1976) 219.
34 W.J. Geary, Coord. Chem. Rev., 7 (1971) 81.