Journal of Organometallic Chemistry, 402 (1991) 133–138
Elsevier Sequoia S.A., Lausanne
JOM 21269

Complexes including acetylides formed from 3-diphenylphosphinocamphor and platinum or palladium

Sarath D. Perera and Bernard L. Shaw *
School of Chemistry, The University, Leeds LS2 9JT (UK)

(Received July 10th, 1990)

Abstract

Treatment of lithiated D-camphor with a half molar equivalent of PPh_2Cl gives the 3-diphenylphosphino enolate anion $[PPh_2(C_{10}H_{14}O)]^-$ as the only phoshorus-containing species. Treatment of lithiated D-camphor with one equivalent of PPh_2Cl gives some of the enolate anion but the main product is the 3-*exo* substituted camphor derivative 3-*exo*-$PPh_2(C_{10}H_{15}O)$ together with some of the 3-*endo*-substituted derivative. On storage of the solution, the 3-*endo* substituted derivative becomes the main product with some of the 3-*exo*-substituted derivative still present. Treatment of a solution of the enolate ion with $Na_2PdCl_4 \cdot 4H_2O$ gives $[Pd\{(PPh_2)C_{10}H_{14}O\}_2]$ or with $PtCl_2$(cyclo-octa-1,5-diene), *cis*-$[Pt\{(PPh_2)C_{10}H_{14}O\}_2]$ is formed. Treatment of these bis-chelate complexes with hydrogen chloride opens up the chelate rings reversibly, giving dichloro-complexes of type $[MCl_2\{(PPh_2)C_{10}H_{15}O\}_2]$ {M = Pd (*trans*-isomer) M = Pt (*cis*-isomer)}. Treatment of ethanol or methanol solutions of these bischelate complexes with acetylenes, especially in the presence of traces of acetic acid also opens up the chelate rings to give di-acetylides of type $[M(C{\equiv}CR)_2\{(PPh_2)C_{10}H_{15}O\}_2]$ {M = Pd or Pt; R = Ph or C(Me) = CH_2}. When treated with HC≡CH or EtC≡CH the bis-chelate $[Pd\{(PPh_2)C_{10}H_{14}O\}_2]$ gives the corresponding acetylides but these could not be isolated and reverted to the starting bis-chelate complex, i.e. acetylide formation is reversible.

Introduction

Phosphino-ketones of type R_2PCH_2COR', or their corresponding enolates of type $[R_2PCH{=}C(O)R']^-$, are capable of bonding of transition metal ions in a number of ways. These phosphino-β-ketonates can bind either as a monodentate ligand (through phosphorus), as in complexes of the type *trans*-$[MCl_2\{Bu^t_2PCH_2COPh\}_2]$ (M = Pd or Pt) [1] or *trans*-$[RhCl(CO)\{Bu^t_2PCH_2COPh\}_2]$ [2] and some complexes of iridium; or phosphino-β-ketones can chelate through phosphorus and through the oxygen of the keto group, e.g. with rhodium(I) and iridium(I) [2]. A more common form of bonding is P,O-chelation through the corresponding enolate ions $[R_2PCH{=}C(O)R']^-$, for which there are many examples, e.g. with nickel [3,4], palladium [1,3], platinum [1,3], rhodium [2] or iridium [2].

In this paper we describe the synthesis of the 3-diphenylphosphino derivative of D- {or (+)}-camphor. Both D- and L- {or (+) and (−), respectively} camphor are readily available and cheap. Moreover, a methylene hydrogen in the 3-position is readily removed by a bulky base such as lithium di-isopropylamide (LDA) at low

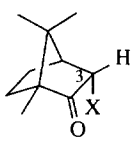
0022-328X/91/$03.50

temperatures to give a carbanion, which reacts with a number of electrophiles, e.g. with methyl iodide it gives a mixture of the *endo*-3-methyl (**1a**) X = Me and the *exo*-3-methyl (**2a**) X = Me derivatives [5,6]. We therefore anticipated that it would be relatively easy to introduce a PPh_2-group into the 3-position of D-camphor by treating the 3-carbanion with Ph_2PCl.

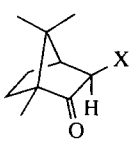
Results and discussion

When we treated D-camphor with lithium di-isopropylamide in THF at −70 °C and then added one half mole equivalent of Ph_2PCl, we obtained a single phosphorus-containing species, (^{31}P-{^1H} NMR evidence) showing a singlet at −32.0 ppm. It was clear from the subsequent chemistry that this species was the enolate ion **3**. When we treated a solution of D-camphor with LDA at −70 °C and added one equivalent of Ph_2PCl, some of the enolate **3** was formed but the ^{31}P-{^1H} NMR spectrum showed two new singlets, at 1.7 and −10.5 ppm due to two other species. With a freshly prepared solution the resonance at 1.7 ppm was more intense than the resonance at −10.5 ppm. After storage of the solution at ca. 20 °C for sixteen hours the resonance at −10.5 ppm had become more intense than the resonance at 1.7 ppm. Since it has been frequently observed that the 3-*exo*-substituted camphor is the kinetic product but that with acid or base this isomerizes to the more stable 3-*endo*-substituted product [5,6], we tentatively assign the ^{31}P-{^1H} resonance at 1.7 ppm to the 3-*exo* product **2b** and the resonance at −10.5 ppm to the 3-*endo* isomer **1b**.

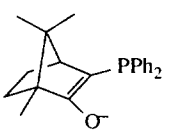
When we treated a methanol solution of $Na_2PdCl_4 \cdot 4H_2O$ with two mole equivalents of the enolate anion **3** we obtained the expected product $[Pd\{(PPh_2)C_{10}H_{14}O\}_2]$ (**4a**). Similarly, treatment of $[PtCl_2$(cyclo-octa-1,5-diene)] with the enolate solution gave the corresponding platinum complex $[Pt\{(PPh_2)C_{10}H_{14}O\}_2]$, **4b**.



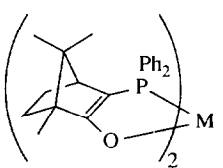
1a X = Me
1b X = PPh_2



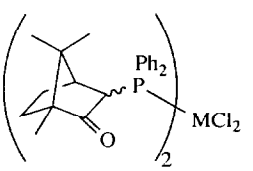
2a X = Me
2b X = PPh_2



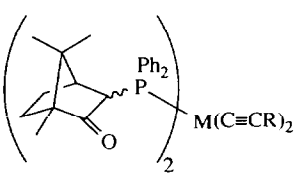
(**3**)



4a M = Pd
4b M = Pt



5a M = Pd
5b M = Pt



6a M = Pd, R = Ph
6b M = Pt, R = Ph
6c M = Pd, R = C(Me)=CH_2
6d M = Pt, R = C(Me)=CH_2

Table 1

IR [a], $^{31}P-\{^1H\}$ NMR [b] and ^1H NMR [c] data

Complex	ν(C=O)	ν(C=C)	ν(C≡C)	ν(M–Cl)	^{31}P		^1H		
					δ(P)	^1J(PtP)	$\delta(CH_3)$	$\delta(C_3-H)$	others
4a		1670 [d]			31.6		0.67s, 1.03s, 1.13s		
4b		1670 [d]			4.6	3645	0.68s, 1.08s, 1.10s		
5a	1725				19.7		0.79s, 0.93s, 0.96s	4.38m	
5b	1725			285,305	6.4	3879	0.79s, 0.88s, 0.88s	5.76m	
6a	1730 [d]		2100 [d]		22.7		0.68s, 0.73s, 0.87s	4.46m	
6b	1725		2105		13.1 [e]	2327 [e]	0.50s, 0.64s, 0.79s	4.35m	
6c	1725		2100		22.4 [e]		0.76s, 0.90s, 0.93s	4.37m	1.43(t, C=C(CH_3)), 4.56(m, C=CH_2)
6d	1730		2105		13.5 [e]	2314 [e]	0.67s, 0.80s, 0.87s	4.26m	1.53(t, C=C(CH_3)), 4.72(m, C=CH_2)

[a] KBr disc ± 2 cm^{-1}. [b] Measured in CH_2Cl_2, in ppm to high field of 85% H_3PO_4, error ± 0.1 ppm. J values ± 1 Hz. [c] Measured in $CDCl_3$. Chemical shifts are in ppm relative to TMS error ± 0.02 ppm. s = singlet, m = multiplet, t = triplet. [d] Nujol mull. [e] Measured in $CDCl_3$.

The formulations for these two complexes follow from the elemental analytical data (see Experimental) and the NMR spectra. In particular, the $^{31}P-\{^1H\}$ NMR pattern for the platinum complex showed a singlet with satellites due to coupling to platinum-195 with $^1J(PtP) = 3645$ Hz. This large coupling constant is typical of phosphorus in *trans*-position to an electronegative atom such as oxygen, e.g. for *cis*-$[Pt\{PPh_2CH{=}C(O)Ph\}_2]$, $^1J(PtP) = 3520$ Hz [3] whilst for *trans*-$[Pt\{PBu^t_2CH{=}C(O)Ph\}_2]$, $^1J(PtP) = 2752$ Hz [1]. Thus the platinum complex **4b** has the *cis*-configuration. We suggest that the palladium complex **4a** also has the *cis*-configuration but we have been unable to confirm this. $[Pd\{PR_2CH{=}C(O)Ph\}_2]$ with R = Ph has the *cis*-configuration but with R = Bu^t the configuration is *trans*, the different configurations are probably, in part, a consequence of the relative steric requirements of the PBu^t_2 and PPh_2 groups. The ^1H NMR data for **4a** and **4b** are given in the Table 1.

We have also studied the action of hydrogen chloride on the bis-chelate complexes **4a** and **4b**. Treatment of dichloromethane solution of the platinum chelate **4b** with dry hydrogen chloride giving a colourless dichloroplatinum(II) complex $[PtCl_2\{(PPh_2)C_{10}H_{15}O\}_2]$ (**5b**) which, from the elemental analysis (Experimental), the large value of $^1J(PtP) = 3879$ Hz (Table 1) and the occurrence of a band at 1725 cm^{-1} due to an uncomplexed ketonic carbonyl group in the camphor residue, is clearly of *cis*-configuration. In the infrared spectrum of **5b** two Pt–Cl stretching vibrations, at 285 and 305 cm^{-1} are indicative of a *cis*-configuration. The palladium bis-chelate complex **4a**, similarly reacted with dry hydrogen chloride to open up the chelate rings and give an adduct $[PdCl_2\{(PPh_2)C_{10}H_{15}O\}_2]$ (**5a**). This was characterized by elemental analysis, a singlet $^{31}P-\{^1H\}$ NMR resonance at 19.7 ppm (Table 1) and a strong $\nu(C{=}O)$ band at 1725 cm^{-1}. However, the far infrared spectrum showed a very strong band at 360 cm^{-1} and no bands in the range 310–250 cm^{-1} suggesting a *trans*-configuration. Treatment of the dichloro-complex **5a** with sodium hydride in THF gave the bis chelate **4a**.

We have also found that the chelate rings in **4a** and **4b** are opened up by the treatment with terminal acetylenes in the presence of acetic acid to give complexes of the type $[M(C{\equiv}CR)_2\{(PPh_2)C_{10}H_{15}O\}_2]$. We have shown that in some cases this chelate ring opening reaction, to give bis-acetylides, is reversible (see below). Without the acetic acid the ring opening occurred much less readily. As an example, **4a** with an excess of phenylacetylene and a trace of acetic acid, the orange solution rapidly faded and became almost colourless. The di(phenylacetylide) complex $[Pd(PPh_2C_{10}H_{15}O)_2(C{\equiv}CPh)_2]$ (**6a**) separated as cream crystals in excellent (> 90%) yield. The platinum complex **6b** was prepared and characterized similarly (see Experimental and Table 1). The platinum diacetylide complex showed a single IR band due to $\nu(C{\equiv}C)$ at 2105 cm^{-1} and in the $^{31}P-\{^1H\}$ NMR spectrum $^1J(PtP)$ is 2327 Hz. *cis*-$[Pt(C{\equiv}CPh)_2(PPh_3)_2]$ has been reported to show a single band due to $\nu(C{\equiv}C)$ at 2125 cm^{-1} [7].

Complexes of the type *trans*-$[Pt(C{\equiv}CPh)_2(PR_3)_2]$, as would be expected, only show one band due to $\nu(C{\equiv}C)$, at ca. 2120 cm^{-1} [8,9]. We have not established whether the stereochemistry of **6a** and **6b** is *cis* or *trans*. We have similarly made the palladium complex **6c** and the platinum complex **6d** of the types $[M(PPh_2C_{10}H_{15}O)_2\{C{\equiv}CC(Me){=}CH_2\}_2]$ (M = Pd or Pt) by treating the bis-chelates of type **4** with the enyne $HC{\equiv}CC(Me){=}CH_2$. Characterizing elemental analytical and NMR data are in Table 1. Both palladium bis-acetylide complexes, i.e. **6a** and

6c slowly reverted to the starting complex **4a** on storage in deuteriochloroform solution. When acetylene was bubbled through a solution of $[\overline{Pd\{(PPh_2)C_{10}H_{14}O\}_2}]$ (**4a**) in acetic acid a single new species was formed characterized by its $^{31}P\text{-}\{^1H\}$ NMR spectrum with $\delta P = 17.9$ ppm. However, on attempted workup this reverted to the starting chelate complex **4a** i.e. the uptake of HC≡CH is reversible. A similar reversible uptake was observed when a dichloromethane/benzene solution of **4a** was treated with ethylacetylene; the bis-ethylethynyl complex formed reversibly had $\delta P = 17.4$ ppm. The platinum complex **4b** when treated with $HC{\equiv}CCH_2OMe$ in ethanol and trace of acetic acid gave a single product, $\delta P = 9.5$ ppm, $^1J(PtP) = 2424$ Hz but on attempts to isolate it reverted to the starting material **4b**. Treatment of the bis-acetylides **6b** or **6d** with dry hydrogen chloride in $CDCl_3$ gave the dichloro-complex **5b**, exclusively (^{31}P NMR evidence).

Experimental

The general techniques and apparatus were the same as described in other recent papers from this laboratory [10].

Generation of 3-diphenylphosphino-D-camphor enolate anion (3)

A solution of D-camphor (3.9 g, 26 mmol) in dry THF (10 cm^3) was added dropwise to a stirred solution of lithium di-isopropylamide (26 mmol) in THF (10 cm^3)/n-hexane (17 cm^3) at −70 °C. After 1.5 h, a solution of chloro(diphenyl)phosphine (2.77 g, 12.5 mmol) in dry THF (15 cm^3) was then added at −70 °C, after which the mixture was allowed to warm up to room temperature. A $^{31}P\text{-}\{^1H\}$ NMR spectrum of the solution showed a single phosphorus resonance at −32.0 ppm, which we assign to the required enolate anion **3**.

A similar experiment in which ca. twice the amount (i.e. one equivalent) of $ClPPh_2$ was added to the lithiated camphor solution gave a final solution which showed three $^{31}P\text{-}\{^1H\}$ singlets, at 1.7, −10.5 and −32.0 ppm; these we tentatively assign to the *exo*-(**2b**), the *endo*-(**1b**) and the enolate ion **3**.

cis-*Bis(3-diphenylphosphino-D-camphor enolate)palladium(II) (4a)*

An excess of the above solution of 3-diphenylphosphino-D-camphor enolate (7.0 cm^3, 1.7 mmol) was added to a solution of $Na_2PdCl_4 \cdot xH_2O$ (0.24 g, 0.75 mmol) in methanol (8 cm^3). After 30 min., water (4 cm^3) was added and the required product was extracted into dichloromethane (15 cm^3). The dichloromethane solution was evaporated to low volume, upon which the required product separated. It formed orange prisms from ethanol. Yield 0.50 g, 86%. (Found: C, 66.95; H, 6.35. $C_{44}H_{48}O_2P_2Pd \cdot C_2H_6O$ calcd.: C, 67.1; H, 6.6%.)

cis-*Bis(3-diphenylphosphino-D-camphor enolate)platinum(II) (4b)*

$[PtCl_2$(cyclo-octa-1,5-diene)] (0.68 g, 1.8 mmol) was added to a stirred solution of 3-diphenylphosphino-D-camphor enolate (4.0 mmol) in THF/n-hexane (17 cm^3), prepared as above. The resultant solution was heated for 2 h at 60 °C, after which it was evaporated to low volume under reduced pressure. Addition of methanol then gave the required product as white microcrystals. Yield 1.25 g, 80%. (Found: C, 59.9; H, 5.8. $C_{44}H_{48}O_2P_2Pt \cdot (CH_4O)$ calcd.: C, 60.2; H, 5.85 %.)

*Bis(3-diphenylphosphino-D-camphor)dichloropalladium(II) (**5a**)*

Dry hydrogen chloride was bubbled through a solution of **4a** (75 mg, 0.096 mmol) in dichloromethane (1.5 cm^3) for 1 min. The resultant solution was stored at ca. 20 °C for 20 h and then evaporated to dryness. The residue was recrystallized from dichloromethane/methanol to give the required product as yellow prisms. Yield 66 mg, 79%. (Found: C, 62.15; H, 5.9. $C_{44}H_{50}Cl_2O_2P_2Pd$ calcd.: C, 62.15; H, 5.95%.)

*Bis(3-diphenylphosphino-D-camphor)dichloroplatinum(II) (**5b**)*

This was prepared in an analogous manner to the palladium complex. It formed white needles from dichloromethane/methanol. Yield 94%. (Found: C, 56.25; H, 5.35. $C_{44}H_{50}Cl_2O_2P_2Pt$ calcd.: C, 56.3; H, 5.35%.)

*Bis(3-diphenylphosphino-D-camphor)diphenylethynylpalladium(II) (**6a**)*

A suspension of the enolate complex **4a** (77 mg, 0.1 mmol) in methanol (5 cm^3) was warmed with acetic acid (25 μL) and an excess of phenylacetylene (74 mg, 0.72 mmol) to ca. 50 °C. The mixture was then put aside at 20 °C. The required product crystallized out as cream needles and was collected, washed with methanol and dried. Yield 92 mg, 93%. (Found: C, 72.4; H, 6.1. $C_{60}H_{60}O_2P_2Pd \cdot (0.25CH_2Cl_2)$ calcd.: C, 72.15; H, 6.1%.)

*Bis(3-diphenylphosphino-D-camphor)diphenylethynylplatinum(II) (**6b**)*

This was prepared and isolated in a similar manner to the analogous palladium complex using ethanol as solvent. Yield 77%. (Found: C, 67.4, H, 5.7. $C_{60}H_{60}O_2P_2Pt$ calcd.: C, 67.35; H, 5.65%.)

*Bis(3-diphenylphosphino-D-camphor)di(3-methylbut-3-en-1-yl)palladium(II) (**6c**)*

This was prepared and isolate in an analogous manner to the phenylethynyl complex using ethanol as solvent. Yield 85%. (Found: C, 71.0; H, 6.55. $C_{54}H_{60}O_2P_2Pd$ calcd.: C, 71.3; H, 6.65%.)

*Bis(3-diphenylphosphino-D-camphor)di(3-methylbut-3-en-1-yl)platinum(II) (**6d**)*

This was prepared and isolated in an analogous manner. Yield 62%. (Found: C, 64.9; H, 6.0. $C_{54}H_{60}O_2P_2Pt$; calcd.: C, 65.0; H, 6.05%.)

Acknowledgements

We thank the S.E.R.C. for support and Johnson Matthey PLC for the generous loan of platinum salts.

References

1 C.J. Moulton and B.L. Shaw, J. Chem. Soc., Dalton Trans., (1980) 299.
2 H.D. Empsall, S. Johnson, and B.L. Shaw, J. Chem. Soc., Dalton Trans., (1980) 302.
3 P. Braunstein, D. Matt, D. Nobel, F. Balegroune, S-E. Bouaoud, D. Grandjean, and J. Fischer, J. Chem. Soc., Dalton Trans., (1988) 353.
4 W. Keim, Nouv. J. Chim., 11 (1987) 531 and references therein.
5 T. Money, Natural Product Reports (1985) p. 253 and references therein.
6 J.H. Hutchinson and T. Money, Can. J. Chem., 62 (1984) 1899.
7 I. Collamati and A. Furlani, J. Organomet. Chem., 17 (1969) 457.
8 J. Chatt and B.L. Shaw, J. Chem. Soc., (1959) 4020.
9 H.D. Empsall, B.L. Shaw and A.J. Stringer, J. Organomet. Chem., 94 (1975) 131.
10 S.W. Carr, B.L. Shaw and M. Thornton-Pett, J. Chem. Soc., Dalton Trans., (1985) 2131.