Journal of Organometallic Chemistry, 132 (1977) 439—443

CYCLOPALLADATION OF VINYLIC OXIMES

BRUCE A GRIGOR * and ALASTAIR J NIELSON
Department of Chemistry, University of Auckland (New Zealand)
(Received December 2nd, 1976)

Summary

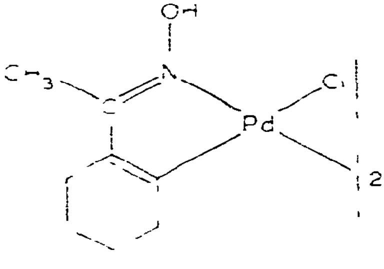
Cyclopalladation of vinylic oximes occurs for the sterically rigid oximes of 1-benzalcyclohexanone and 1-acetylcyclohexene giving dimeric complexes which retain the alkene double bond The presence of the vinylic palladium bond is shown both by spectroscopic methods and cleavage reactions using carbon monoxide or cyanide ion The complexes do not make good substrates for the synthesis of vinylic oxime derivatives.

Introduction

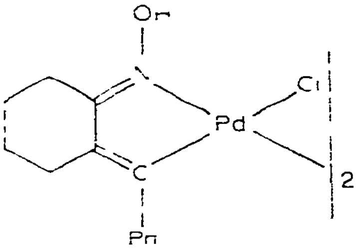
Intramolecular cyclopalladation (ortho-metallation [1]) of aromatic nitrogen ligands is well established e g for azobenzenes [1] and ketoximes [2], but hitherto there has been no report of cyclopalladation of vinylic nitrogen ligands Cyclometallation of such ligands occurs for rhodium [3] and rhenium [4] with 2-vinylpyridine, for iridium with vinylazobenzenes [5], and for platinum with *N,N*-dimethyl-2-methylallylamine [6] Reactions of palladium salts with allylamines [7] and 2-vinylpyridine [8] in methanol result in methoxypalladation products, and azocyclohexenes give complexes of the *trans*-$PdCl_2L_2$ type [9] The absence of cyclopalladated vinylic nitrogen ligands is not due to any thermodynamic instability, as vinylic-palladium complexes are known [10], but the instability of palladium(IV) complexes may result in palladium reacting by routes other than the oxidative addition (and reductive elimination) routes suggested for platinum, iridium and rhodium

Results and discussion

Our attempts to form palladium—vinyl carbon bonds by the reaction of lithium tetrachloropalladate with E-vinyl oximes such as methyl vinyl ketoxime, 3-pentene-2-one oxime and benzalacetone oxime in methanol with, or without, added sodium acetate, resulted in $PdCl_2L_2$ complexes or unidentified products Using the more sterically rigid 1-acetylcyclohexene oxime and 1-benzalcyclohexanone oxime (with which co-ordination of nitrogen to palladium would bring the metal closer to the vinylic hydrogen), the analytically pure cyclopalladated products. I and II, were obtained in over 90% yield by adding a slight excess of lithium tetrachloropalladate in methanol to an equimolar solution of E-oxime and sodium acetate in methanol, the mixture being stirred vigorously at the onset of precipitation In the absence of sodium acetate, complex I was formed in high yield, while no precipitation of II occurred after 2 days.



(I)



(II)

In both I and II, ν(OH) was shifted to higher wave number (3420 cm^{-1}) compared with the free E-oxime, while ν(C=N) shifted to slightly lower wave numbers (I, 1623, II, 1625 cm^{-1}), characteristic of nitrogen lone pair donation as found for ortho-palladated aryloxime complexes [2] Free ligand absorbances in the 400—900 cm^{-1} region, attributed to trisubstituted alkenes, were absent in complexes I and II, and there was also present a new absorption in the 1540—1545 cm^{-1} region, similar to that found for cyclometallated arenes, where it is varyingly attributed to ν(C=C) [11], aromatic benzene ortho-disubstitution [12], and metal—aryl bonds [13]. Proton nuclear magnetic resonance spectra (60 MHz) of I and II indicated loss of the vinylic-hydrogen signals found for the corresponding free oximes (for free oxime of I, δ = 6.15, for free oxime of II, δ = 6 85 ppm from $(CH_3)_4Si$) and the hydroxyl-H absorption was moved upfield 2 ppm compared with the free ligands The ^{13}C NMR spectrum of II in $CDCl_3$ showed the expected four quaternary carbon signals (δ = 168.9, 168 3, 143 4, 132 7 ppm from $(CH_3)_4Si$), with that furthest downfield being tentatively assigned to C_{vinyl}—Pd by comparison with the free ligand spectrum, and those reported for C_{vinyl}—Rh (185 97 ppm) [3] and C_{vinyl}—Ir (161 88 ppm) [5]

Confirmation that the double bond of the ligand remained intact was obtained by carrying out cleavage reactions on both complexes Carbonylation in deuteromethanol-d_1 and sodium deuteroxide, followed by hydroxyl proton back exchange and preparative TLC, incorporated deuterium at the carbon previously attached to palladium In general about 25% of the recovered oxime was undeuterated using undried carbon monoxide and an undeuterated oxime hydroxyl group In the presence and absence of palladium metal, the reaction conditions gave no deuterium exchange at the vinylic hydrogen when carried out on the free ligand The method is milder than the normal lithium aluminium deuteride reduction used by Onoue [2] for cyclometallated aryl oximes where reduction of the oxime azomethine bond occurred, and also eliminates possible carbon to nitrogen migration which can occur with this hydridic reagent [14]

Preliminary results with di-μ-chlorobis[α-(dimethylamino)-*o*-tolyl]-di-palladium [15] indicate that the method may be extended to arene cyclopalladated compounds. In further establishing the presence of the double bond the complexes were reacted with sodium cyanide in aqueous methanol, the cleavage resulting in the free ligands.

Attempted reactions on the palladium—vinylic carbon bond showed that these complexes containing the vinylic oxime ligand do not make good substrates for substitution reactions Carbonylation in methanol gave organic products which were not stable to air and were not further characterised, while reaction of I and II with *m*-chloroperbenzoic acid in benzene solution [16] gave many products

Methyl lithium in benzene solution, which gives methyl substituted aromatic compounds with cyclopalladated arene complexes [17], and substituted alkenes with palladium vinyl complexes [18] (prepared from $Pd(Ph_3P)_3$ and alkenyl halides), reacted with II returning the free oxime both in the presence and absence of triphenylphosphine

Hydrogenation of either complex in ethyl acetate at atmospheric pressure gave palladium metal and the free ligand with no apparent hydrogenation of the double bond as found for hydrogenations of palladium complexes containing both σ and π-olefin bonds [19]. At higher pressure many side products were obtained, possibly as a consequence of hydrogenation of the oxime functional group in the presence of palladium metal [20]

Experimental section

IR spectra were recorded on Perkin—Elmer 237 or 337 spectrophotometers using KBr discs and ^1H NMR spectra were measured on a Varian T-60 spectrometer (data expressed as ppm from TMS) ^{13}C NMR spectra were recorded on a Jeol FX 60 spectrometer (ppm from TMS) and mass spectra were determined on a Varian-MAT CH 7 mass spectrometer Preparative TLC was carried out on 1 mm thick plates of Kieselgel $PF_{254+366}$ (Merk) Carbonylations were carried out in a $\frac{1}{4}$ inch thick pyrex reaction vessel equipped with pressure gauge and inlet and outlet tap Carbon monoxide was Matheson Co , C P grade, water content approximately 10 p p m

Complex I

To a solution of anti-1-acetylcyclohexene oxime (0 6 g, 4 3 mmol) in methanol (5 ml) was added lithium tetrachloropalladate (1 13 g, 4 3 mmol) in methanol (10 ml) and the solution was stood for 3 days at room temperature during which time yellow crystals precipitated The solid was filtered, crushed to a fine powder, washed with methanol (3 ml), ether (10 ml) and dried at 100°C Yield 91%, m p. 160—165°C decomp (Found C, 34 07, H, 4 30, N, 4 88, Cl, 12 91 $(C_8H_{12}ClNOPd)_2$ calcd.: C, 34 29; H, 4 25, N, 5 00, Cl, 12.68%) IR 3420 (OH), 1623 (C=N), 1047 (N—O) ^1H NMR (DMSO-d_6) δ, 1 38—1 64 (m, 4 H, $C_{4,5}$-methylenes), 1 89 (s, 3 H, Me), 2.0—2 23 (m, 2 H, C_3-methylene), 2.30—2.64 (m, 2 H, C_6-methylene), 9 90 (s, 1 H, OH).

Reductive carbonylation The complex (0 2 g, 0 35 mmol) was carbonylated in deuteromethanol-d_1 (3 ml) and sodium deuteroxide (0.25 g) at 40 p s i at room temperature for 30 min The solution was filtered, poured into water, neutralised with dilute hydrochloric acid, extracted with ether and the solvent removed from the dried ($MgSO_4$) organic layer The residue was dissolved in methanol, stirred for 10 min and the solvent removed This back-exchange process was carried out twice Purification of this product by preparative TLC ($CHCl_3$/silica gel) gave 1-acetyl-2-deuterocyclohexene oxime (yield 83%), Mass spec.. M^+ found, 140, $M^{+\cdot}$ calcd.. 140 ($d_0 = 29$, $d_1 = 71\%$).

Cleavage with cyanide. The complex (0 06 g, 0 1 mmol) was suspended in methanol (5 ml) and NaCN added (ca 3 mol excess) The solution was stirred for 1 hour and the solvent removed in vacuo Preparative TLC of the residue gave 1-acetylcyclohexene oxime (yield 71%) with identical m p., IR and ^1H NMR spectra to that of an authentic sample

Complex II

Methanol (approx. 45 ml) was added to 1-benzalcyclohexanone oxime (7 0 g, 34 mmol) and sodium acetate (2 87 g, 34 mmol) until the heated solution did not precipitate solid on standing at room temperature for 5 min To this solution was added lithium tetrachloropalladate (9 9 g. 37 mmol), in methanol (25 ml) and further methanol was added to dissolve any solid The solution was allowed to stand until the product first appeared and then stirred vigorously for 30 min The solid was washed and dried as before Yield 95% M p 175—177°C decomp Found. C, 45.30, H, 4.47, N, 3 69, Cl, 10 86. $(C_{13}H_{14}ClNOPd)_2$ calcd · C, 45 63, H. 4 12, N, 4 09, Cl, 10 37%. IR· 3410 (OH), 1625 (C=N), 1025 (N—O), 748, 693 (mono-substituted benzene). ^1H NMR (DMSO-d_6)· δ 1.20—1 67 (m, 4 H, $C_{4\ 5}$-methylenes), 1 90—2 20 (t, 2 H, C_3-methylene), 2.42—2 68 (m, 2 H, C_6-methylene), 6 84—7.31 (m, 5 H aromatics), 10 40 (s, 1 H, OH) ^{13}C NMR ($CDCl_3$) ppm from TMS Methylenes· 21 557, 23 635, 25 582, 27 401 Tertiary carbons 126 356, 126 875, 127.525 Quaternary carbons 132.719, 143 368, 168 296, 168 950

The complex was carbonylated in deuteromethanol-d_1 and sodium deuteroxide as described for I giving, on purification, 1-benzal-7-deuterocyclohexanone oxime (60%) Mass spec. M^+ found 202, M^+ calcd 202 (d_0 32%, d_1 68%). Cleavage of the complex with sodium cyanide gave the free ligand (86%)

Hydrogenations general procedure

The complex I or II was suspended in ethyl acetate and stirred while hydrogen was introduced at atmospheric pressure. After 3 hours the solution was filtered from palladium metal and the ligand purified by preparative TLC to give the free oxime in greater than 90% yield

Reaction with methyl lithium

To a dry benzene solution of the 1-benzalcyclohexanone oxime complex (0.4 g, 0.58 mmol) and triphenylphosphine (0 30 g, 1 1 mmol) was added methyl lithium (2 34 mmol) in ether. The mixture was stirred for 1 h, aqueous methanol added and the solvent mixture removed Preparative TLC of the residue gave 1-benzalcyclohexanone oxime. (Yield 70%). In the absence of triphenylphosphine the free oxime was again regenerated using this procedure

References

1 G W Parshall, Accounts Chem Res , 3 (1970) 139
2 H Onoue K Minami and K Nakagawa Bull Chem Soc Japan, 43 (1970) 3480
3 R J Foot and B T Heaton J Chem Soc Chem Commun (1973) 838
4 M I Bruce, B L Goodall and I Matsuda Austral J Chem 28 (1975) 1259
5 J F van Baar, K Vrieze and D J Stufkens J Organometal Chem 85 (1975) 249
6 J M Kliegman and A C Cope J Organometal Chem 16 (1969) 309
7 A C Cope, J M. Kliegman and E C Friedrich J Amer Chem Soc , 89 (1967) 287
8 A Kasahara, K Tanaka and T Izumi Bull Chem Soc Japan 42 (1969) 1702
9 L Caglioti, L Cattalini, F Gasparrini, G Marangoni and P A Vigato, J Chem Soc (A) (1971) 324
10 T Yukawa and S Tsutsumi, Inorg Chem 7 (1968) 1458 W A Bennett P W Clark, G B Robertson and P O Whimp J Organometal Chem 63 (1973) C15
11 J M Duff and B L Shaw J Chem Soc Dalton (1972) 2219
12 A J Cheney B E Mann B L Shaw and R M Slade J Chem Soc (A) (1971) 3833
13 D M Adams, Metal-Ligand and Related Vibrations, Edward Arnold, London, 1967 p 184
14 M Harfenist and E. Magnien J Amer Chem Soc 80 (1958) 6080
15 A C Cope and E C Friedrich J Amer Chem Soc 90 (1968) 909
16 cf Yu A Ustynyuk I V Barinov and E I Sirotkina Doklady Akad Nauk U S S R 187 (1969) 112
17 cf S -I Murahashi Y Tanba M Yamamura and I Moritani Tetrahedron Lett (1974) 3749
18 M Yamamura I Moritani and S -I Murahashi J Organometal Chem 91 (1975) C39
19 J K Stille and R A Morgan J Amer Chem Soc 88 (1966) 5135 G Paiaro, A De Renzi and R Palumbo Chem Commun (1967) 1150
20 P A S Smith Open-chain Nitrogen Compounds W A Benjamin Inc New York 1966 Vol 2 p 60