Cyclopalladation of 1-Tetralone (3,4-Dihydronaphthalen-1-one) Oximes

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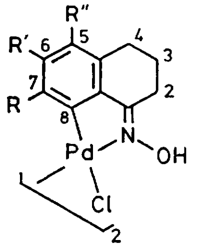
Cyclopalladated complexes precipitate from methanolic $Li_2[PdCl_4]$–$Na[O_2CMe]$ solutions containing 1-tetralone oxime, the 6-methoxy-analogue, and the 7-substituted derivatives, substituent R = CH_3–, CH_3CH_2–, MeO–, but reaction fails when R = $(CH_3)_2CH$–, $(CH_3)_3C$–, or $-NO_2$. The oxime derivatives of methyl 12-methoxy-7-oxopodocarpa-8,11,13-trien-19-oate and methyl 7-oxopodocarpa-8,11,13-trien-19-oate readily metallate while the oxime of methyl 7-oxoabieta-8,11,13-trien-18-oate does not. Carbonylation of the cyclopalladated 1-tetralone oxime complexes in methanol gives the corresponding 8-methoxycarbonyl-1-tetralone oximes. Hydrogen-1 n.m.r. analysis of 1-tetralone oxime and $Li_2[PdCl_4]$ solutions show $[PdCl_2(oxime)_2]$ is not a reaction intermediate. At −76 °C co-ordinated oxime exhibits a downfield shift for H^8, characteristic of above-plane geometry of the ligand, while at 0 °C an upfield shift relative to the free oxime suggests in-plane geometry. The intermediate is isolable in water giving *cis*-$[PdCl_2(oxime)]\cdot 3H_2O$ which on redissolving gives the soluble cyclometallated species [PdCl(*CN*-oxime)(S)] (S = solvent) and HCl by an irreversible process. Dimerisation gives [{PdCl(*CN*-oxime)}$_2$] or the complex [PdCl(*CN*-oxime)L] in the presence of L (L = oxime or PPh_3).

CYCLOPALLADATION reactions[1] have been shown from studies of ligand substituent effects to be electrophilic at the metal centre,[2] but few aspects of the mechanism are known. To obtain a fuller understanding of the processes involved in cyclopalladations of aromatic ketoximes,[3] the reactions of 1-tetralone oximes were studied and the effects of deactivating and potential sterically hindering substituents examined. The study was extended to naturally occurring diterpenoid compounds.

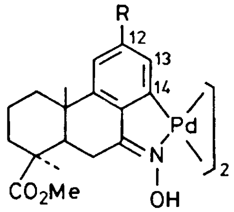
RESULTS AND DISCUSSION

Preparation of Complexes.—The reaction of platinum and palladium salts with aromatic ketoximes has led to a variety of complexes containing metallated and nitrogen-only bound oxime.[3] In the present study, a mixture of lithium tetrachloropalladate, 1-tetralone oxime, and sodium acetate (1 : 1 : 1) in methanol gave complex (7) containing both metallated and nitrogen-only bound oxime while the fully metallated dimer (1) was obtained from two equivalents of $PdCl_4^{2-}$. A ^1H n.m.r. spectrum of the $Li_2[PdCl_4]$ showed it to contain sufficient water of hydration to reduce the effective concentration of palladium needed to form (1). Subsequent use of 1.2 equivalents of $PdCl_4^{2-}$ in concentrated solutions gave the best yield and cleanest product. Using these conditions complex (6) was obtained from 7-hydroxyiminopodocarpa-8,11,13-trien-19-oate in 96% yield.

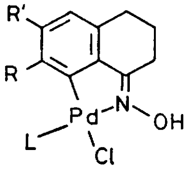
In a study of steric effects of alkyl substituents at C^7, reactions with 3,5-dimethyl- and 7-ethyl-1-tetralone oximes led to complexes (2) and (3) while the 7-isopropyl and 7-t-butyl compounds failed to give a precipitate, as did the oxime derivative of methyl dehydroabietate (isopropyl group at C^{13}). Hydrogen-1 n.m.r. spectra obtained after removal of solvent from these mixtures showed many products. Reaction of 7-ethyl-1-tetralone oxime with less than one equivalent of $PdCl_4^{2-}$ gave complex (8) with the 7-isopropyl and t-butyl substituted compounds again failing to give precipitates. 7-Methoxy-1-tetralone oxime gave an impure product for which the Pd–C bond was established from i.r. and ^1H n.m.r. spectra. Other studies have shown that methoxy-groups do not effect the cyclopalladation of *NN*-dimethyl-3,5-dimethoxybenzylamine,[4] whereas *NN*-3,5-tetramethylbenzylamine gave a *trans*-$[PdCl_2L_2]$ complex.[5]



(1) R = R' = R'' = H
(2) R = R'' = Me, R' = H
(3) R = Et, R' = R'' = H
(4) R = R'' = H, R' = OMe



(5) R = OMe
(6) R = H



(7) R = R' = H, L = 1-tetralone oxime
(8) R = Et, R' = H, L = 7-ethyl-1-tetralone oxime
(9) R = R' = H, L = PPh_3
(10) R = H, R' = OMe, L = C_2D_6SO

With 7-nitro-1-tetralone oxime an insoluble *trans*-$[PdCl_2L_2]$ complex was formed which could not be induced to metallate on refluxing in methanolic $Na[O_2CMe]$. The nitro-group would impart an unfavourable steric interaction on the reaction in addition to deactivating the C^8 position. However, both 7-hydroxyimino-12-methoxypodocarpa-8,11,13-trien-19-oate (known to be highly deactivated towards electrophilic substitution at C^{14} [5]) and 6-methoxy-1-tetralone oxime gave high yields of complexes (5) and (4) in the normal reaction period.

Infrared Spectra.—The complexes show similar i.r. spectra to the known acetophenone complexes [3] [*i.e.* ν(OH) shifted 200 cm^{-1} higher and ν(C=N) shifted 30 cm^{-1} lower compared with the free ligand]. Absorptions occurring between 1 500 and 1 600 cm^{-1} are attributed in other metal–aryl carbon complexes to ν(C=C),[6] aromatic *ortho* disubstitution,[7] and metal–aryl carbon bonds [8] but are also shown for cyclopalladated vinylic oxime complexes [9] so that they probably arise from an increase in conjugation. Phenyl group absorptions in these regions are absent or weak but gain intensity on conjugation.[10] Other features of the cyclometallated oxime are a shift in ν(N–O) of the free ligand (960 cm^{-1} region) to higher wavenumber (*ca.* 40 cm^{-1}) and tentatively assigned absorptions of the new aromatic ring substitution (800 cm^{-1} region, out-of-plane C–H deformation). The latter bands have been assigned for cyclopalladated imine complexes.[11]

Physical data for cyclopalladated aromatic oxime complexes

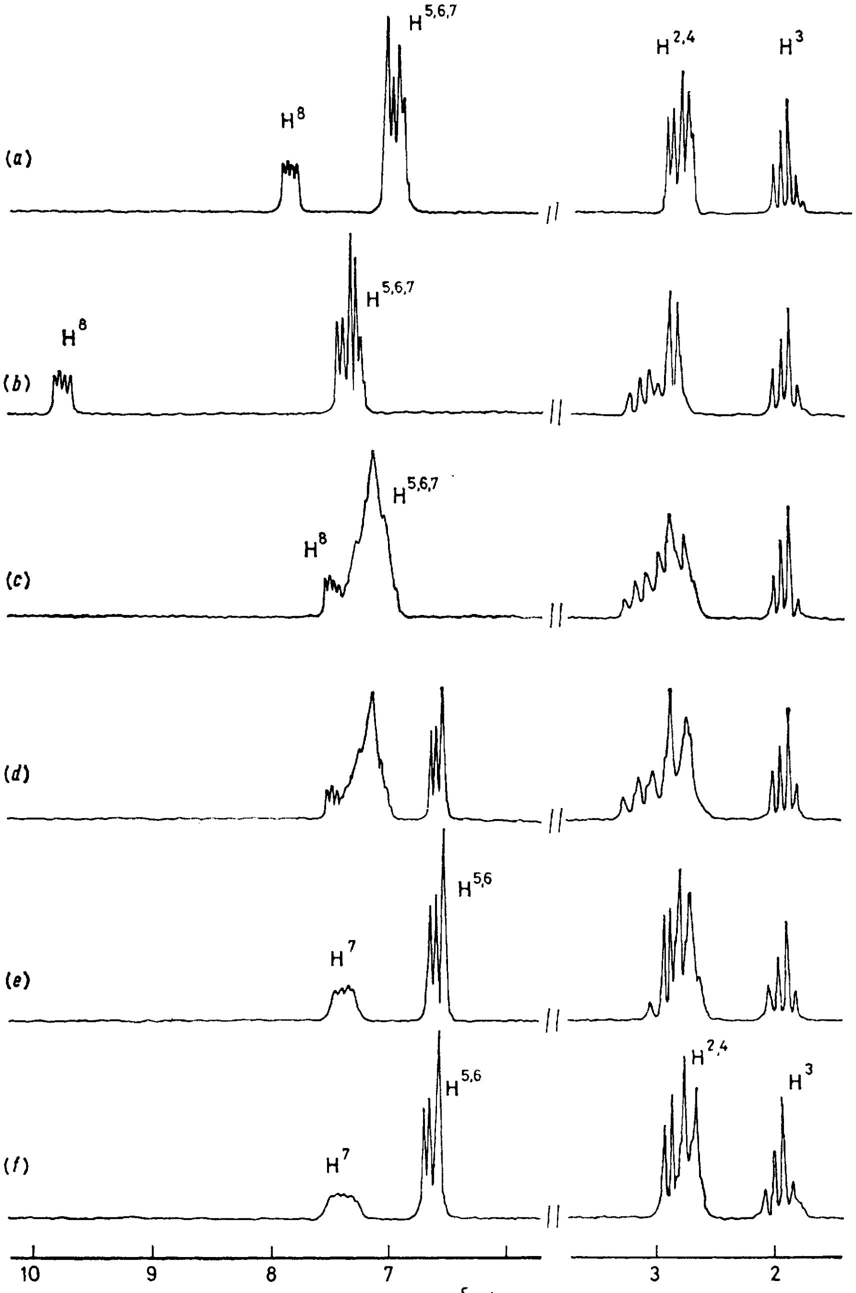
Complex	Yield (%)	Decomp. pt. (θ_c/°C)	Analyses [a] (%)				I.r. spectra [b] (cm^{-1})			^{1}H n.m.r. spectra [c,d] (δ)	
			C	H	N	Cl	ν(C=C)	ν(NO)	aromatic substitution [e]	aromatics	OH [b]
(1) $[\{PdCl(C_{10}H_{10}NO)\}_2]$	96	302	39.8 (39.7)	3.5 (3.4)	4.8 (4.7)	11.9 (11.7)	1 558	1 050 *965*	768, 720, 570 (1, 2, 3)	6.9 (m, $H^{5,6}$), 7.45 (b, H^7)	10.0 *11.3*
(2) $[\{PdCl(C_{12}H_{14}NO)\}_2]$ [f]	94	170	43.4 (43.6)	4.2 (4.3)	4.1 (4.2)	11.3 (10.8)	1 540 *1 600*	1 035 *960*	*g*	6.6 (s, H^6)	10.45 *11.32*
(3) $[\{PdCl(C_{12}H_{14}NO)\}_2]$ [h]	83	188	44.8 (43.6)	4.6 (4.3)	4.4 (4.2)	10.6 (10.8)	1 542 *1 608*	1 002 *960*	560 (1, 2, 3, 4)	6.8 (s, $H^{5,6}$)	10.3 *11.0*
(4) $[\{PdCl(C_{11}H_{12}NO_2)\}_2]$	92	182	39.9 (39.8)	3.6 (3.6)	4.1 (4.2)	10.7 (10.7)	1 550	1 035 960	855, 560 (1, 2, 3, 5)	6.58 (d, H^5) 7.15 (b, H^7)	9.8 *11.1*
(5) $[\{PdCl(C_{19}H_{24}NO_4)\}_2]$	82	230	48.1 (48.3)	5.3 (5.1)	2.8 (3.0)	7.5 (7.5)	1 550 *1 608*	*g*	845, 581 (1, 2, 3, 5)	6.6 (d, H^{11}), 7.1 (b, H^{13})	9.9 *10.4*
(7) $[PdCl(C_{10}H_{10}NO)(C_{10}H_{11}NO)]$	63	209	50.5 (51.8)	4.7 (4.6)	6.2 (6.0)	7.6 (7.7)	1 573 *1 600*	1 160, *988* *965*	770, 570 (1, 2, 3) 740, 550, 489 (1,2)	6.9 (m, $H^{5,6}$), 7.45 (b, H^7) 7.14 (m, $H^{5,6,7}$), 7.85 (m, $H^{8'}$)	10.5, 11.3 *11.3*
(8) $[PdCl(C_{12}H_{14}NO)(C_{12}H_{15}NO)]$	61	148	55.8 (55.5)	5.8 (5.6)	5.2 (5.4)	7.1 (6.9)	1 560 *1 608*	1 015, 993 *960*	572 (1, 2, 3, 4) 820, 460 (1, 2, 4)	6.7 (m, $H^{5,6}$) 7.0 (m, $H^{5',6}$) 7.7 (m, $H^{8'}$)	10.41, 11.0 *11.0*
(9) $[PdCl(C_{10}H_{10}NO)(PPh_3)]$ [i]	84	204 [j]	58.4 (59.6)	4.5 (4.5)	2.4 (2.5)	6.4 (6.3)	1 575, 1 555	994 *965*	*g*	6.16 (d, H^7), 6.42 (2d, H^6) 6.7 (d, H^5) $J = 8$ Hz	10.43 *11.3*
(10) $[PdCl(C_{11}H_{12}NO_2)(C_2D_6SO)]$ [k]	90	158 [j]	36.5 (37.5)	4.2 (5.8)	3.1 (3.3)	8.8 (8.5)	1 558 *1 602*	1 020 *960*	860, 550		
(11) $[PdCl_2(C_{10}H_9N_2O_3)_2]$	90	180	41.2 (40.9)	3.5 (3.1)	9.3 (9.5)	12.6 (12.1)	1 608 *1 602*	980 *962*	*g*		

[a] Calculated figures are given in parentheses. [b] Free-ligand values are italicised. [c] Data for [$^2H_6$]dmso solutions. [d] Assignment given in parentheses, s = singlet, d = doublet, m = multiplet, b = broad. [e] Tentative assignment only. [f] 3,5-Dimethyl-1-tetralone oxime. [g] Assignment undetermined. [h] 7-Ethyl-1-tetralone oxime. [i] P = 5.7% (5.5). [j] Melting point. [k] S = 7.7% (7.7).

*Hydrogen-*1 *N.M.R. Spectra.*—In [$^2H_6$]dmso the *ortho* metallation was shown from the absence of the C^8 proton resonance and upfield shift of the hydroxyl proton (see Table). For complexes (1) and (6) the H^7 resonance occurs downfield from those of H^5 and H^6 as shown by the absence of this feature in the C^7 substituted compounds, but for (6) in $CDCl_3$, H^7 absorbs slightly upfield from the other aromatics. A similar assignment is given tentatively for the proton adjacent to the Pd–C bond in cyclometallated complexes of monosubstituted aromatic nitrogen ligands.[3,4,12]

In [$^2H_6$]dmso the dimeric complexes exhibited broadened resonances for the hydroxyl and C^7 proton where relevant. Addition of several drops of D_2O or MeOD to a solution of (1) caused the aromatic resonances to become a deceptively simple ABX system (*i.e.* 1 : 2 : 1 triplet for H^7 and 1 : 1 doublet for H^5 and H^6) while addition of excess of water led to reprecipitation of (1). After dissolving the 6-methoxy-1-tetralone oxime complex (4) the [$^2H_6$]dmso bridge-split complex (10) precipitated from solution but a similar compound could only be obtained from (1) after refluxing and isolating the product in water. Cryoscopic molecular-weight determinations of (1) in dimethyl sulphoxide (dmso) gave low values for a monomeric species but evidence for bridge splitting did come from the ^{1}H n.m.r. spectrum of (7) which contained the aromatic and hydroxyl proton resonances of (1) and free oxime in a ratio of 1 : 1. Thus both (1) and (7) appear to exist in dmso as solvent stabilised monomers, the broadening effect most likely arising from rapid exchange of loosely bound dmso molecules. The appearance of free oxime in (7) probably results from a destabilising metal–proton interaction inherent in the complex (see later).

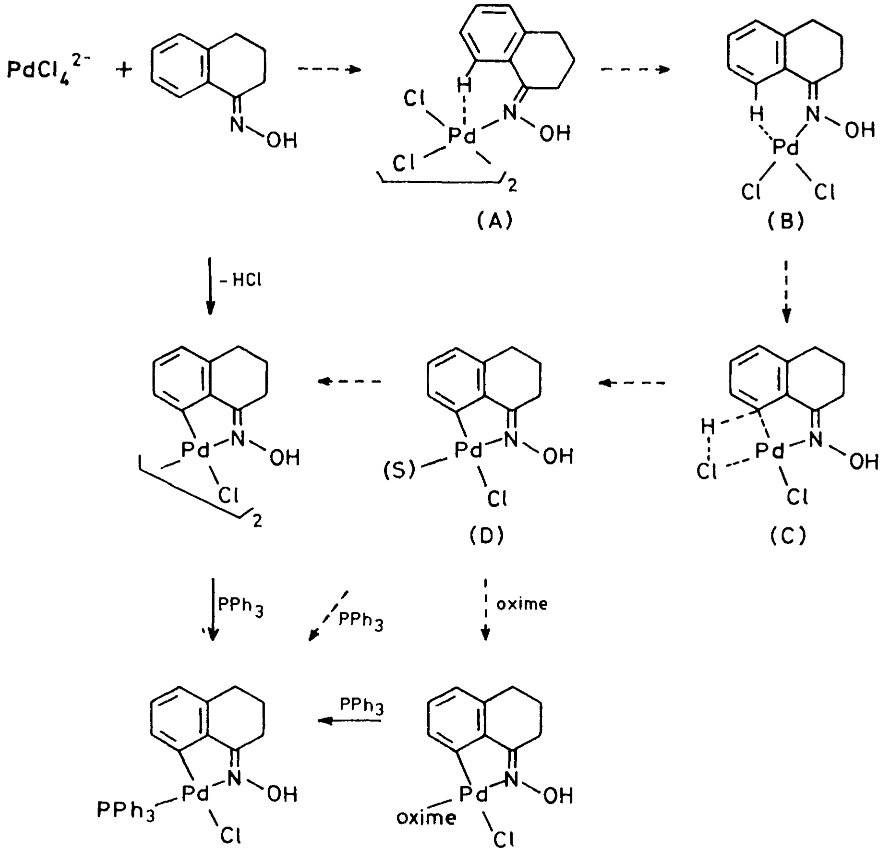
Carbonylations.—Treatment of complexes (1) or (3) with CO in methanol gave 8-methoxycarbonyl-1-tetralone oximes along with cleaved oxime (30—50%). From chloroform solution the unstable complexes [PdCl(CO)(*CN*-oxime)] [13] were isolated which gave the oxime ester compounds on further carbonylation in MeOH. For complex (3) where the ethyl substituent at C^7 could sterically hinder CO insertion, carbonylation occurred at a lower pressure with less ligand cleavage (<20%). Unsubstituted oximes were obtained from the C^{14} electron-deficient complex (5) and from (1) in acetic acid or methanolic sodium hydroxide, while in MeOD–Na[OD] solution the complexes gave C^8 or C^{14} deuteriated oximes. This reaction is superior to that using Li[AlD$_4$] for deuterium incorporation since it does not reduce the C=N function and has been used in characterising cyclopalladated vinylic oxime complexes.[9]



Hydrogen-1 n.m.r. analysis of the reaction of 1-tetralone oxime and Li$_2$[PdCl$_4$] in CD$_3$OD. (*a*) 1-Tetralone oxime alone, (*b*) 1-tetralone oxime and Li$_2$[PdCl$_4$] at −50 °C (resonances broad at −78 °C), (*c*) at 0 °C, (*d*) at 20 °C, (*e*) complex (1) precipitating from solution, and (*f*) complex (1) in [$^2H_6$]dmso

Mechanism.—Hydrogen-1 n.m.r. spectra in CD$_3$OD of the 7-isopropyl and 7-t-butyl substituted oxime reaction mixtures showed immediate nitrogen co-ordination from changes in the $C^{2,4}$ methylene resonances, and the existence of an above-plane configuration for

H^8 from a large downfield shift of its resonance.[14] No change occurred on standing. In the absence of $Na[O_2CMe]$ 1-tetralone oxime mixed with $PdCl_4^{2-}$ at −78 °C gave a similar spectrum but the downfield shift of H^8 persisted only to 0 °C after which a series of spectral events occurred resulting in precipitation of (1) (see Figure). Attempts to isolate an anionic species $[PdCl_3(oxime)]^-$ as proposed in Parshall's mechanism [15] by addition of cations such as $[NPr^n_4]Cl$ (known to precipitate $[PdCl_3(CO)]^-$) [16] or $[PPh_4]Cl$ led to $[PdCl_4][cation]_2$ and cleaved oxime. Yellow *trans*-$[PdCl_2(PPh_3)_2]$ and cleaved oxime were obtained by adding PPh_3. A reaction stoicheiometry of 1 : 1 was shown from the uncomplexed oxime present in an ^1H n.m.r. spectrum of oxime and $PdCl_4^{2-}$ mixed in a ratio of 2 : 1.2 so that the intermediate is not a *trans*-$[PdCl_2L_2]$ complex (which cyclometallates on refluxing for L = azobenzene [17]). As yet the intermediate remains uncharacterised but it is proposed that if an anion is not present, a dimer of the form $[\{PdCl_2(oxime)\}_2]$ (A) (see Scheme) may account for the ^1H n.m.r. features. Results of work presently in progress indicate that the shift recorded for H^8 may be characteristic of dimeric species. The existence of $[(PdCl_2L)_2]$ where L = *o*-*NN*-dimethylaminotoluene is claimed [18] but similar compounds are known only for phosphine and arsine ligands.[19]



Scheme S = Solvent

At 0 °C a yellow compound was isolated in water which analysed as $[PdCl_2L]\cdot 3H_2O$, L = 1-tetralone oxime. The i.r. spectrum showed *cis*-Pd–Cl stretches at 338 and 324 cm^{-1} with absorptions at 3 500 and 1 630 cm^{-1} suggesting lattice water only. The ^1H n.m.r. spectrum was identical to that of the reaction mixture of 0 °C at which temperature the H^8 resonance moved upfield [spectrum (*c*)]. Ligand planarity imposes a close proximity of the C^8 proton and metal for co-ordination of the *anti* oxime nitrogen, without involvement of π aromatic orbitals, so that with loss of above-plane geometry in (A), the interaction could then lie in or about the square plane. A shielding effect is predicted for protons in this environment [20] and has been observed for a methyl resonance in $[IrHCl\{(CH_3)_2C_6H_2\text{-}N{=}NC_6H_2(CH_3)_2\}]$.[21] Extreme instability towards metallation has not allowed full characterisation of the intermediate but on the available evidence it is proposed to be *cis*-$[PdCl_2L]$, L = 1-tetralone oxime, (B). *X*-Ray studies, however, have shown that planar ligands can distort to remove proximity effects [22] so that the C^8 proton may not completely cover the fourth co-ordination position. A species involving co-ordinated H_2O cannot be ruled out on the basis of the i.r. spectrum alone.

In the ^1H n.m.r. at −80 °C, (B) did not reconvert to

(A) and no downfield shift of H^8 was observed, suggesting that free rotation about the Pd–N bond does not occur: while the shift of H^8 would be close to that of the free ligand for such a process, the population of above- or below-plane rotamers should increase as the temperature decreases.[23] Why (A) converts to (B) is not clear but if the metal–proton interaction in (A) is destabilising towards dissociation of the proposed dimer, rotation into the plane could easily occur. The interaction is unlikely to be sufficient to displace Cl^- from an intermediate of the form $[PdCl_3(oxime)]^-$.

At 20 °C an i.r. spectrum of the reaction mixture showed the 1 540 cm^{-1} band of the metallated complex, a ^1H n.m.r. spectrum contained the $H^{5,6}$ multiplet of (1) and the resonances of (B) [spectrum (*d*)], and before precipitation of (1) commenced, addition of PPh_3 gave (9) and 1-tetralone oxime in yields consistent with the ratio of soluble cyclometallated species (D) (probably solvent stabilised) and intermediate (B) shown in the ^1H n.m.r. spectrum.

The transformation of (B) to (D) is apparently irreversible as no C^8 deuteriated oxime was recovered after reaction with PPh_3. Use of 1-tetralone oxime and the 8-deuterio-analogue ($^2H_0$ 44%, $^2H_1$ 56%) in MeOH gave a slight decrease in the $^2H_0$ compound ($^2H_0$ 37%, $^2H_1$ 63%) but the difference probably arises from a kinetic isotope effect rather than a redistribution of deuterium atoms. Reversibility in other cyclopalladations has not been studied but it is noted that the reaction for imines with $Pd(O_2CMe)_2$ readily occurs in $MeCO_2H$.[24]

The metallation process was not indicated by the ^1H n.m.r. spectra but it is apparent from the C^7 isopropyl and t-butyl substituted oximes that formation of (B) allows the C^8 proton to experience an environment (*i.e.* $d_{x^2-y^2}$ orbitals) suited to an electrophilic process. The failure of complexes of Ir, Rh, Pt, and Pd containing above-plane metal–proton interactions to cyclometallate electrophilically[25] may thus be related to an inability to form intermediates similar to (B). However in other complexes, metallation is not an immediate consequence of protons approaching or moving through the coordination plane.[23,26] A close approach of the C^8 proton and chlorine present in (B) would facilitate proton abstraction so that in the absence of a Wheland intermediate or oxidative addition, a concerted process as in (B) $\longrightarrow$ (C) may best account for the metallation. Thus for the deactivated C^{14} position of methyl 7-hydroxyimino-12-methoxypodocarpa-8,11,13-trien-19-oate a low-energy route would exist for elimination of H^+.

For the final reaction product, L (L = oxime or PPh_3) in the presence of (D) gave the complex [PdCl(*CN*-oxime)L], while in the absence of L dimerisation gave (1). The overall rate of reaction was much faster in the presence of $Na[O_2CMe]$.

EXPERIMENTAL

Analytical data were obtained by the Microanalytical Department, Imperial College, and Professor A. D. Campbell and associates, University of Otago, New Zealand. Melting points were determined on a Reichert Kofler Hotbench or Kofler hot-stage apparatus and are uncorrected. Infrared spectra were recorded on Perkin-Elmer 237, 337, and 457 instruments on KBr discs or Nujol mulls between NaCl or CsCl plates. Hydrogen-1 n.m.r. spectra were recorded at 60 MHz on Perkin-Elmer R-12, Varian T-60 spectrometers, and on a JEOL FX 60 spectrometer, using a proton probe, and mass spectra were obtained on a VG-7070 instrument. Preparative thin layer chromatography (t.l.c.) was carried out on 1-mm thick plates of Kieselgel $PF_{245\,+\,366}$ (Merck). Carbonylations were carried out in a 6.4-mm thick Pyrex reaction vessel equipped with pressure gauge and an inlet and outlet tap. Carbon monoxide was Matheson Co., C. P. grade, water content approximately 10 p.p.m. Substituted 1-tetralones were prepared by known procedures[27] and the corresponding oximes prepared in ethanolic hydroxylamine hydrochloride–Na[OH] solutions. Lithium tetrachloropalladate was dried and stored at 100 °C.

Di-μ-chloro-bis(1-*tetralone oxime*-C,N)*dipalladium*, (1).—The preparation of this compound is typical of the dimeric complexes in general. To a solution of lithium tetrachloropalladate (1.0 g, 38 mmol) in methanol (5 cm^3) was added 1-tetralone oxime (0.5 g, 31 mmol) and sodium acetate (0.25 g, 31 mmol) in methanol (10 cm^3). After standing for 2 h, the precipitated solid was filtered off, crushed to a fine powder, washed with methanol and diethyl ether, and dried at 70 °C.

I.r. (Nujol) bands at 3 419 (OH), 1 630 (C=N), 1 558 (C=C, conj.), 1 050 (N–O), 768, 720, and 570 cm^{-1} (1,2,3-trisubstituted benzene). ^1H n.m.r. δ([$^2H_6$]dmso) 1.95 (m, 2,[†] C^3 methylene), 2.74 (m, 4, $C^{2,4}$ methylenes), 6.90 (m, 2, $C^{5,6}$ aromatics), 7.40 (b, 1, C^7 aromatic), and 10.0 (b, 1, OH).

Chloro(1-*tetralone oxime*-C,N)(1-*tetralone oxime*-N)*palladium*(II), (7).—The preparation for this complex is as above except that 1-tetralone oxime (0.5 g, 31 mmol) and sodium acetate (0.25 g, 31 mmol) in methanol (20 cm^3) were added to lithium tetrachloropalladate (0.81 g, 0.31 mmol) in methanol (5 cm^3).

I.r. (Nujol) bands at 3 225, 2 160 (OH), 1 641, 1 650 (C=N), 1 573 (C=C, conj.), 1 050, 988 (N–O), 740, 550, 489 (1,2-disubstituted benzene), 851, 770, and 570 cm^{-1} (1,2,3-trisubstituted benzene). ^1H n.m.r. δ([$^2H_6$]dmso) 1.82 (m, 4, C^3 methylene), 2.72 (m, 8, $C^{2,4}$ methylene), 6.90 (m, 2, $C^{5,6}$ aromatics), 7.14 (m, 3, $C^{5',6',7'}$ aromatics), 7.50 (m, 1, C^7 aromatic), 7.85 (m, 1, $C^{8'}$ aromatic), 10.50 (b, 1, OH), and 11.30 (s, 1, OH).

Carbonylations.—The reactions of CO with di-μ-chloro-bis(1-tetralone oxime-*C*,*N*)dipalladium are typical for the other complexes.

1\. The complex (0.8 g, 13 mmol) was suspended in dry methanol and treated with CO at 100 p.s.i.[*] for 2 h at 85 °C during which time palladium metal was precipitated. The filtered solution was concentrated *in vacuo* (50 °C) and the components separated by preparative t.l.c. ($CHCl_3$) giving 1-tetralone oxime (0.24 g, 60%) and 8-methoxycarbonyl-1-tetralone oxime (0.18 g, 32%), m.p. 148—150 °C (Found: C, 65.8; H, 6.1; N, 6.4. $C_{12}H_{13}NO_3$ requires C, 65.7; H, 6.0; N, 6.4%).

I.r. (Nujol) bands at 3 220 (OH), 1 732 (C=O, ester), 1 635 (C=N), 1 262 (C–O–C), 960 (N–O), and 845 cm^{-1} (1,2,3-

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[*] 1 lbf in^{-1} (p.s.i.) $\approx 7.09 \times 10^3$ Pa.

[†] This figure is the number of H atoms for each resonance; b = broad.

trisubstituted benzene). ^{1}H n.m.r. δ(CCl_4) 1.95 (m, 2, C^3 methylene), 2.80 (m, 4, $C^{2,4}$ methylenes), 3.80 (s, 3, CO_2Me), 7.20 (s, 3, $C^{5,6,7}$ aromatics), and 9.0 (b, 1, OH).

Under similar conditions, the 7-ethyl-1-tetralone oxime complex gave 7-ethyl-8-methoxycarbonyl-1-tetralone oxime (73%) ($M^{\cdot+}$, Found: 247. $C_{14}H_{17}NO_3^{\cdot+}$ requires 247).

I.r. bands at 3 380 (OH), 1 700 (C=O, ester), and 960 cm^{-1} (N–O). ^{1}H n.m.r. δ($CDCl_3$) 1.21 (t, 3, Me), 1.80 (m, 2, C^3 methylene), 2.64 (m, 6, $C^{2,4,11}$ methylenes), 3.85 (s, 3, OMe), and 7.14 (s, 2, $C^{5,6}$ aromatics).

2. A solution of the 1-tetralone oxime complex (1) (0.3 g, 0.49 mmol) in [$^2H_5$]pyridine (0.5 cm^3) and [$^2H_1$]methanol (3 cm^3) was stirred for 15 min and the solvent removed. The process was repeated twice (100% OD by ^{1}H n.m.r.). The residue was suspended in [$^2H_1$]methanol (4 cm^3) containing sodium deuterioxide (0.2 g) and treated with CO at 40 p.s.i. for 30 min at room temperature. The palladium was filtered off, the filtrate poured into water, and the solution neutralised with dilute HCl followed by extraction with diethyl ether. The organic layer was washed several times with water, dried over Mg[SO_4], and the solvent removed. Back exchange of the monodeuteriated oxime was carried out several times in methanol and the solvent removed. Purification of the residue by preparative t.l.c. ($CHCl_3$) gave 8-deuterio-1-tetralone oxime (0.11 g, 68%) [$M^{\cdot+}$, Found: 162. $C_{10}DH_{10}NO^{\cdot+}$ requires 162. $^2H_0$ = 26, $^2H_1$ = 74, $^2H_2$ = 0%. ^{1}H n.m.r. δ(CCl_4), H^8 *ca.* 20, OH, 100%].

Methyl 7-*Hydroxyiminopodocarpa*-8,11,13-*trien*-19-*oate*.—This compound was obtained from methyl 7-oxopodocarpa-8,11,13-trien-19-oate (prepared by CrO_3–$MeCO_2H$ oxidation of methyl podocarpa-8,11,13-trien-19-oate [28]) by reaction with hydroxylamine hydrochloride and pyridine in ethanol. M.p. 145—147 °C (Found: C, 71.7; H, 7.6; N, 4.4. $C_{18}H_{23}NO_3$ requires C, 71.7; H, 7.7; N, 4.6%).

I.r. bands at 3 250 (OH), 1 728 (C=O, ester), 1 625 (C=N), 940 (N–O), and 750 cm^{-1} (1,2,3-trisubstituted benzene). ^{1}H n.m.r. δ($CDCl_3$) 1.0 (s, 3, C^{10} Me), 1.32 (s, 3, C^4 Me), 3.75 (s, 3, CO_2Me), 7.29 (m, 3, $C^{11,12,13}$ aromatics), 7.29 (m, 1, C^{14} aromatic), and 8.90 (b, 1, OH).

Di-μ-chloro-bis(*methyl* 7-*hydroxyiminopodocarpa*-8,11,13-*trien*-19-*oate*-C,N)*dipalladium*, (6).—The oxime (0.6 g, 1.9 mmol) and sodium acetate (0.16 g, 1.9 mmol) in methanol (10 cm^3) were added to lithium tetrachloropalladate in methanol (10 cm^3) and the product filtered off, washed, and dried. M.p. 230 °C (decomp.).

I.r. bands at 3 425 (OH), 1 620 (C=N), 1 550 (C=C, conj.), 1 014 (N–O), 778, 741, and 538 cm^{-1} (1,2,3-trisubstituted benzene). ^{1}H n.m.r. δ([$^2H_6$]dmso) 0.98 (s, 3, C^{10} Me), 1.23 (s, 3, C^4 Me), 3.64 (s, 3, CO_2Me), 7.0 (m, 2, $C^{11,12}$ aromatics), 7.40 (m, 1, C^{13} aromatic), and 10.25 (b, 1, OH). δ($CDCl_3$) 1.02 (s, 3, C^{10} Me), 1.26 (s, 3, C^4 Me), 3.66 (s, 3, CO_2Me), 6.70 (m, 1, C^{13} aromatic), 7.12 (m, 2, $C^{11,12}$ aromatic), and 8.15 (b, 1, OH).

The complex was stirred in $CHCl_3$–[$^2H_1$]methanol solution for 10 min and the solvent removed. The process was repeated several times and the residue carbonylated in [$^2H_1$]methanol–sodium deuterioxide solution as before. Work-up and purification gave methyl 14-deuterio-7-hydroxyiminopodocarpa-8,11,13-trien-19-oate (34 mg, 65%) [$M^{\cdot+}$, Found: 302. $C_{18}DH_{22}NO_3^{\cdot+}$ requires 302. $^2H_0$ = 33, $^2H_1$ = 67, $^2H_2$ = 0%. ^{1}H n.m.r. δ($CDCl_3$), H^{14}, *ca.* 25, OH, 100%].

Chloro(*hexadeuteriodimethyl sulphoxide*)(6-*methoxy*-1-*tetralone oxime*C,N)*palladium*(II) (10).—Complex (4) was dissolved in [$^2H_6$]dmso and the solution allowed to stand. The solid was filtered off and washed with benzene and diethyl ether.

I.r. (Nujol) bands at 3 420 (OH), 1 558 (C=C, conj.), 1 020 (N–O), 860, and 550 cm^{-1} (1,2,4-trisubstituted benzene).

Dichloro(1-*tetralone oxime*)*palladium–Water* (1/3).—This complex was prepared by mixing equimolar methanolic solutions of 1-tetralone oxime and lithium tetrachloropalladate at 0 °C and pouring the reaction mixture into iced water. The yellow solid was collected and dried *in vacuo* for 0.1 h at room temperature and stored at −78 °C under argon {Found: C, 30.6; H, 3.2; Cl, 17.0; N, 3.5. [$PdCl_2$-($C_{10}H_{11}NO$)]·$3H_2O$ requires C, 30.6; H, 4.3; Cl, 18.0; N, 3.6%}.

I.r. bands at 3 350 (H_2O), 3 170 (oxime, OH), 1 630 (H_2O), 980 (N–O), 338, and 324 cm^{-1} (*cis*-$PdCl_2$). The complex is unstable towards metallation on standing or on dissolving in CH_2Cl_2 or methanol. The mass spectrum gives only the molecular ion of the free ligand and the u.v. spectrum shows no change from the free ligand or Li_2[$PdCl_4$]. Reaction with PPh_3 in hot MeOH or CH_2Cl_2 gave yellow *trans*-[$PdCl_2(PPh_3)_2$] and 1-tetralone oxime which was purified by preparative t.l.c. ($CHCl_3$).

Hydrogen-1 *N.M.R. Studies on Complex Formation*.—In general, the reactants were mixed in [$^2H_4$]methanol and the ^{1}H n.m.r. spectra run immediately. In the case of 1-tetralone oxime, the reactants were mixed at −76 °C and placed in the spectrometer, held at this temperature. Precipitated complexes were identified by spectral comparison with authentic samples.

Reaction Reversibility Determination.—1-Tetralone oxime (40 mg, 0.25 mmol) was dissolved in [$^2H_1$]methanol, the solution stirred, and the solvent removed. The exchange process was carried out three times (OD = 100% by ^{1}H n.m.r.). The process was repeated with lithium tetrachloropalladate (80 mg, 0.30 mmol) in D_2O and the residue dried at 100 °C. The components were mixed in [$^2H_4$]methanol (0.41 cm^3) and the reaction monitored to the stage of spectrum (*d*), Figure, at which point PPh_3 in warm MeOD was added. The precipitate of [PdCl(1-tetralone oxime-*C*,*N*)-(PPh_3)] was filtered off and dried *in vacuo*, m.p. 204—205 °C (decomp.). I.r. bands at 3 100 (OH), 1 590 (C=N), 1 575 cm^{-1} (C=C conj.). ^{1}H n.m.r. δ($CDCl_3$) 1.90 (m, 2, C^3 methylene), 2.80 (m, 4, $C^{2,4}$ methylenes), 6.4 (m, 3, $C^{5,6,7}$ aromatics), 7.55 (m, 15, PPh_3), and 10.64 (b, 1, OH). [The complex was also prepared by adding PPh_3 to the cyclometallated complex (1) in CH_2Cl_2.]

Preparative t.l.c. ($CHCl_3$) of the filtrate gave 1-tetralone oxime (52%) ($M^{\cdot+}$, Found: 161. $C_{10}H_{11}NO^{\cdot+}$ requires 161. $^2H_0$ = 100, $^2H_1$ = 0%).

The reaction was repeated using a mixture of 1-tetralone oxime and 8-deuterio-1-tetralone oxime ($^2H_0$ = 44.2, $^2H_1$ = 55.8% by mass spectroscopy) in CH_3OH. At the onset of precipitation of the cyclopalladated complex (1), PPh_3 in warm methanol was added and the oxime worked up as before ($^2H_0$ = 36.7, $^2H_1$ = 63.3%).

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