Transition-metal–Carbon Bonds. Part 45.[1] Attempts to Cyclopalladate Some Aliphatic Oximes, *NN*-Dimethylhydrazones, Ketazines, and Oxime *O*-Allyl Ethers. Crystal Structures of $[Pd_2\{CH_2C(CH_3)_2C(=NOH)CH_3\}_2Cl_2]$ and $[Pd\{CH_2C(=NNMe_2)C(CH_3)_3\}(acac)]$ †

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E-Methyl t-butyl ketoxime, with sodium acetate and $Na_2[PdCl_4]$ in methanol, cyclopalladates regiospecifically on a t-butyl methyl to give the chloride-bridged complex $[Pd_2\{CH_2C(CH_3)_2C(=NOH)CH_3\}_2Cl_2]$ (1a), the crystal structure of which has been determined (see below). The corresponding bromide and iodide complexes have been made, as have several mononuclear species by bridge-splitting reactions, *e.g.* of type $[Pd\{CH_2C(CH_3)_2C(=NOH)CH_3\}X(L)]$ (X = Cl or Br; L = CO, PMe_2Ph, PPh_3, or pyridine). The salts $[Pd\{CH_2C(CH_3)_2C(=NOH)CH_3\}(Ph_2PCH_2CH_2PPh_2)]X$ (X = I or BPh_4) have also been prepared. *E*-Ethyl t-butyl and *E*-phenyl t-butyl ketoximes are similarly cyclopalladated, but oximes of other carbonyl compounds, *e.g.* trimethylacetaldehyde, methyl isopropyl ketone, diisopropyl ketone, ethyl methyl ketone, or 2-methylcyclohexanone, give dark intractable products. In contrast, methyl t-butyl *NN*-dimethylhydrazone with $Na_2[PdCl_4]$ and $Na[O_2CMe]$ cyclometallates regiospecifically on the single methyl group to give $[Pd_2\{CH_2C(=NNMe_2)Bu^t\}_2Cl_2]$. The corresponding bromide or iodide complexes have been made as have bridge-split derivatives (with PMe_2Ph, PPh_3, or pyridine) and also an acetylacetonate, $[Pd\{CH_2C(=NNMe_2)Bu^t\}(acac)]$ (6), the crystal structure of which has been determined. *NN*-Dimethylhydrazones of acetaldehyde, acetone, cyclohexanone, or 4-t-butylcyclohexanone cause decomposition on attempted cyclopalladation. Acetophenone *NN*-dimethylhydrazone cyclopalladates specifically on the 2 position of the benzene ring (*i.e.* not on the *C*-methyl group). Methyl t-butylketazine cyclopalladates specifically on a t-butyl methyl giving $[Pd_2\{CH_2C(CH_3)_2C(=NN=CMeBu^t)CH_3\}_2Cl_2]$: dimetallation could not be effected. Acetoxime *O*-allyl ether in methanol is cyclopalladated with concomitant attack by OMe to give $[Pd_2\{CH(CH_2OCH_3)CH_2ON=C(CH_3)_2\}_2Cl_2]$. The corresponding ethoxy-compound is formed in ethanol; cyclohexanone oxime *O*-allyl ether is similarly palladated. Crystal data are: (1a), Monoclinic, space group $P2_1/c$, a = 7.312(1), b = 8.539(2), c = 28.478(4) Å, β = 91.74(1)°, and Z = 4; (6), Triclinic, space group $P\bar{1}$, a = 9.573(3), b = 10.714(3), c = 8.983(2) Å, α = 94.41(2), β = 113.76(2), γ = 104.65(2)°, and Z = 2.

ORGANOPALLADIUM compounds are very versatile and are increasingly used in synthesis and catalysis.[2-9] We set out to increase the range of such compounds available to the synthetic chemist, attempting to palladate simple derivatives of saturated aliphatic ketones or aldehydes. The cyclometallation of a saturated aliphatic carbon atom is generally much more difficult to achieve than that of an aromatic carbon (*ortho*-metallation), which is now common.[3,4] Prior to our work, part of which has been published in a preliminary communication,[10] the only examples of saturated aliphatic carbons on nitrogen donors which had been cyclopalladated were with 8-methyl- and 8-ethyl-quinoline.[11,12]

We chose to study first oximes and dimethylhydrazones: the oximato- (=NOH) and dimethylhydrazonato- (=$NNMe_2$) groups have been much used as protecting groups in organic chemistry.[13,14] Oximes and dimethylhydrazones are readily converted back into the parent carbonyl compounds.[14] The nitrogens of these two protecting groups would co-ordinate to palladium(II) and we hoped a cyclopalladation reaction would follow. Several oximes of aromatic aldehydes and ketones have been *ortho*-palladated[15] as have vinylic oximes.[16] Oximes often exist as stable *E* and *Z* isomers, the energy barrier to rotation about the C=N bond being high. There thus seemed a good possibility of completely regiospecific cyclopalladation depending on which isomer was used. Dimethylhydrazones have a lower energy barrier to rotation around C=N and usually the *E* and *Z* isomers interconvert at a rate sufficient to prevent isolation of the separate isomers. However, either of the two nitrogens (=N or NMe_2) could act as a donor and, since cyclometallation would be expected to give a five-membered chelate ring, cyclometallation on either side of the C= atom could occur, depending on which nitrogen is preferred.

RESULTS AND DISCUSSION

We chose first to study the oxime of methyl t-butyl ketone (pinacolone) which exists solely in the *E* configuration. We reasoned that on co-ordination of the palladium by the nitrogen at least one of the t-butyl methyls must be held in close proximity to the palladium, a requirement for metallation. Steric and conformational effects were shown by us to be important in the cyclometallation of tertiary phosphines[17] and have been much used since then. Treatment of sodium tetrachloropalladate(II) with *E*-methyl t-butyl ketoxime in methanol in the presence of sodium acetate gave the hoped for cyclopalladated product (1a) as orange needles in good (>70%) yield. Cyclopalladation was slow, taking *ca.* 3 d at 25 °C and did not seem to occur in the absence of sodium acetate. Microanalytical and characterizing data are in Table 1 and i.r. and n.m.r. data are in Table 2. The binuclear complex (1a) gave a mass spectrum

† Di-μ-chloro-bis[(3-hydroxyimino-2,2-dimethylbutyl-C^1N)-palladium(II)] and (3,3-dimethyl-2-NN-dimethylhydrazonobutyl-C^1N)pentane-2,4-dionatopalladium(II), respectively.

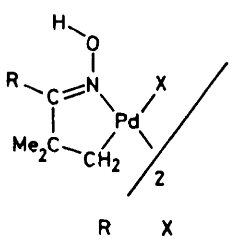
TABLE 1

Microanalytical [a] and molecular-weight [b] data

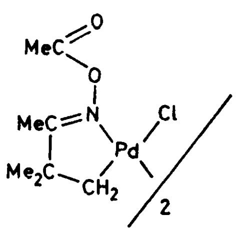
Compound	Analysis (%) C	H	N	Halogen	M
(1a)	28.6 (28.15)	4.75 (4.7)	5.55 (5.45)	14.1 (13.85)	522 (512)
(1b)	24.2 (24.0)	3.95 (4.05)	4.4 (4.65)	26.75 (26.6)	
(1c)	21.0 (20.75)	3.3 (3.5)	3.95 (4.05)	36.75 (36.5)	
(2)	32.5 (32.25)	4.65 (4.75)	4.7 (4.7)	12.05 (11.9)	616 (596)
(3b)	43.05 (42.65)	5.6 (5.85)	3.2 (3.55)	9.5 (9.00)	382 (394)
(3c)	55.8 (55.6)	5.15 (5.25)	2.9 (2.7)	6.6 (6.85)	493 (518)
(3d)	39.9 (39.4)	5.2 (5.1)	8.45 (8.35)	10.2 (10.6)	345 (335)
(3e)	51.6 (51.2)	4.75 (4.85)	2.9 (2.5)	15.1 (14.2)	
(3f)	38.6 (38.35)	5.45 (5.3)	3.4 (3.2)	18.8 (18.2)	
(1d)	31.5 (31.15)	5.3 (5.25)	5.25 (5.2)	13.25 (13.15)	532 (540)
$EtC(=NOH)Bu^t$	62.25 (65.05)	11.6 (11.7)	10.8 (10.85)		120 (129)
(1e)	41.8 (41.55)	4.6 (4.45)	4.5 (4.4)	11.35 (11.15)	621 (636)
(3g)	56.7 (56.4)	5.5 (5.5)	2.65 (2.65)	6.4 (6.65)	
(3h)	59.9 (60.0)	4.7 (5.0)	2.45 (2.4)	6.3 (6.1)	
(4a)·$0.5CH_2Cl_2$	51.5 (51.5)	4.95 (4.85)	1.85 (1.90)	16.7 (17.0)	
(4b)	69.0 (69.2)	5.95 (5.8)	1.40 (1.45)		
$[Pd\{CH_3C(=NOH)C(CH_3)_3\}_2Cl_2]$	35.55 (35.35)	6.4 (6.4)	7.2 (6.85)	17.4 (17.4)	419 (408)
(5a)	33.75 (33.95)	5.95 (6.05)	9.65 (9.9)	13.2 (12.5)	582 (566)
(5b)	29.7 (29.35)	5.2 (5.25)	8.4 (8.55)	24.7 (24.4)	
(5c)	26.4 (25.65)	4.8 (4.6)	7.35 (7.5)	33.2 (33.7)	
(6)	45.1 (45.05)	6.95 (7.0)	8.15 (8.1)		358 (347)
(7a)	57.7 (57.25)	6.1 (5.9)	5.05 (5.15)	6.6 (6.5)	526 (545)
(7b)	46.0 (45.6)	6.4 (6.7)	6.65 (6.65)	7.55 (8.4)	414 (241)
(7c)	53.4 (52.95)	5.35 (5.45)	4.8 (4.75)	13.9 (13.55)	601 (590)
(7d)	41.2 (41.25)	5.95 (6.05)	5.85 (6.0)	17.35 (17.15)	451 (466)
(7e)	43.05 (43.1)	5.85 (6.1)	11.3 (11.6)	10.2 (9.8)	
(8b)	72.45 (72.15)	6.3 (6.35)	3.50 (2.9)		
(9)	39.8 (39.65)	4.25 (4.3)	9.3 (9.25)	12.0 (11.7)	621 (606)
(10a)	42.9 (42.75)	7.0 (6.9)	8.15 (8.3)	10.65 (10.5)	643 (674)
(10b)	38.0 (37.8)	6.35 (6.1)	7.25 (7.35)	20.7 (20.95)	749 (763)
(10c)	33.9 (33.65)	5.35 (5.4)	6.8 (6.55)	30.25 (29.6)	827 (857)
(11)	59.8 (60.1)	6.45 (6.4)	4.85 (4.65)	6.1 (5.9)	609 (599)
(14a)	29.1 (29.4)	4.9 (4.95)	4.65 (4.9)	12.8 (12.4)	
(14b)	31.55 (32.0)	5.3 (5.35)	4.5 (4.65)	12.15 (11.8)	
(14c)	37.1 (36.85)	5.45 (5.55)	4.35 (4.3)	11.1 (10.85)	

[a] Calculated values shown in parentheses. [b] Determined in chloroform on a Hitachi–Perkin-Elmer apparatus.

with the most intense peak at $m/e = 512$, as expected, and the remaining m/e pattern for the molecular ion in good agreement with that calculated from the relative isotopic abundances.



	R	X
(1a)	Me	Cl
(1b)	Me	Br
(1c)	Me	I
(1d)	Et	Cl
(1e)	Ph	Cl



(2)

The structure of this binuclear complex, determined by X-ray diffraction, is shown in Figure 1, and bond lengths are given in Table 3. The molecule approximates C_s symmetry with the nitrogen atoms mutually *cis* with respect to the di-μ-chloro-bridge. This leads to a large difference between the lengths of the bonds to Cl(1) which is *trans* to nitrogen-donor atoms and those to Cl(2) which is *trans* to carbon. There is also a considerable folding of the Pd_2Cl_2 ring leading to a short Pd(1) · · · Pd(2) distance of 2.991(1) Å.

The binuclear bridged chloro-complex readily gave the corresponding bridged bromo- (1b) or iodo- (1c) complexes on metathesis. On treatment with acetic anhydride the hydroxyl groups were acetylated to give the corresponding diacetate (2). The chlorine bridging system was reversibly split by carbon monoxide to give a colourless, labile, carbonyl derivative (3a) which, on heating or in solution, readily lost carbon monoxide to give back the chloro-bridged dimer (1a). The bridging system was split by tertiary phosphines, *e.g.* PMe_2Ph or PPh_3, or by pyridine to give the mononuclear complexes (3b), (3c), or (3d) respectively. For the tertiary phosphine complexes, ^1H and ^{31}P n.m.r. spectroscopy established that only one isomer was produced but from

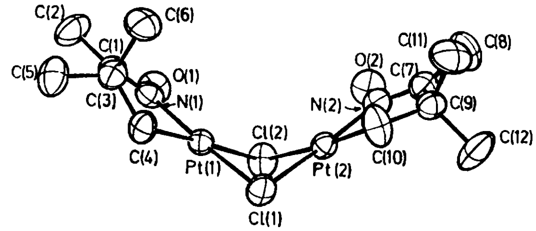


FIGURE 1 ORTEP drawing of the molecular structure of (1a). Thermal ellipsoids are shown at the 50% probability level

TABLE 2

Infrared (cm^{-1}),[a] and ^1H [b] and ^{31}P [c] n.m.r. data

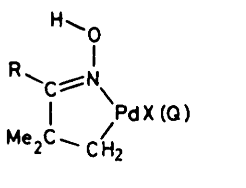
	I.r.			^1H N.m.r.				^{31}P N.m.r.
Compound	ν(Pd–Cl)	ν(C=N)	ν(OH)	$PdCH_2$	$C(CH_3)$	$C(CH_3)_2$	OH	δ(P)
(1a)	238m, 297s	1 650vw	3 380vs, 3 420vs	2.5	1.82	1.15	8.15	
(1b)		1 655vw	3 330vs, 3 360vs	2.55	1.84	1.18	8.10	
(1c)		1 650vw	3 350vs, 3 370 (sh)	2.55	1.84	1.19	7.9	
(1d)	240m, 300s	1 645w	3 400vs, 3 360vs	2.5		1.15	8.05	
(1e) [d]	243m, 298s	1 640vw	3 405vs, 3 315vs	2.8	0.90	0.9	*e*	
(2)	221m, 293s	1 625vw		2.35	1.78	1.24		
(3a)				2.56	1.88	1.25	9.98	
(3b) [f]	232m, 278m? [g]		3 180vs	1.76 (d) *J*(PH) = 4	1.10	1.05	9.87 (d) *J*(PH) = 2.5	5.5
(3c) [f]	223m, 252m, 280m? [g]	1 670	3 060vs, 3 150vs	1.70 (d) *J*(PH) = 4	1.9	1.05	10.46 (d) *J*(PH) = 2.5	34.35
(3d) [f]	284m	1 605s, [h] 1 650vw, 1 670w	3 040vs, 3 090vs, 3 150vs	2.3	1.83	1.18	10.05	
(3e) [f]		1 670w	3 060vs, 3 190vs	1.78 (d) *J*(PH) = 4	1.9	1.05	10.02 (d) *J*(PH) = 2.5	56.35
(3f) [f]		*i*	3 205vs	1.82 (d) *J*(PH) = 4	1.88	1.10	9.95 (d) *J*(PH) = 2.5	8.15
(3g)	282s	*i*	3 100vs, 3 160vs	1.7 (d) *J*(PH) = 4		1.05	10.4 (d) *J*(PH) = 3.5	
(3h)	255	1 573vw	3 050vs, 3 175vs	1.85 (d) *J*(PH) = 4		1.10	10.55 (d) *J*(PH) = 3	
(4a)		*i*	*i*	1.90 (dd) *J*(PH) = 7, 3.8	2.16	1.16	*i*	34.7 (d), 53.1 (d) *J*(PP) = 27
(4b)		*i*	*i*	1.92 (dd) *J*(PH) = 7, 3.8	1.85	1.1	*i*	37.05, 53.5 *J*(PP) = 26
$[PdQ_2Cl_2]$ [j]	343s	1 645w	3 260vs		2.7	1.2	8.7	
					$C(CH_3)_2$	$N(CH_3)_2$		
(5a)	255s, 304s	1 620w, 1 642s		3.15	1.02	2.86		
(5b)		1 620w, 1 642s		3.20	1.05	2.92		
(5c)		1 620w, 1 642s		3.2	1.15	2.98		
(6) [k]		*i*		2.95	1.15	2.82		
(7a)	285m	1 630m, 1 642s		2.12 (d) *J*(PH) = 3.5	0.90	2.98 (d) *J*(PH) = 2.5		33.85
(7b)	283m	1 626s, 1 640m		2.35 (d) *J*(PH) = 3.5	1.15	2.85 (d) *J*(PH) = 2.5		4.45
(7c)		1 628m, 1 640s		2.23 (d) *J*(PH) = 3.5	0.90	3.03 (d) *J*(PH) = 2.5		34.4
(7d)		1 626m, 1 636m		2.43 (d) *J*(PH) = 3.5	1.05	2.90 (d) *J*(PH) = 2.5		3.93
(8b)		1 625br		2.68 (dd) *J*(PH) = 6.6, 3.5	1.05	2.5 (br)		38.75 (d), 55.8 (d) *J*(PP) = 24.5
(9)	247m, 267m	1 620m			2.42 (CH_3)	2.75		
					$C(CH_3)_2$	$C(CH_3)$	$C(CH_3)_3$	
(10a)	222s, 297s	1 615vs		2.30 (br d)	1.18	1.60, 2.13 (br d)	1.15	
(10b)		1 615vs		2.30 (br d)	1.15	1.58, 2.15 (br d)	1.02	
(10c)		1 612vs		2.28 (br d)	1.18	1.60, 2.03 (br d)	1.15	
(11) [f]	282w	1 635s		1.10	1.26	1.74, 2.04	1.26	35.05

[a] Spectra recorded as Nujol mulls: v = very, s = strong, m = medium, w = weak, sh = shoulder, br = broad. [b] Recorded at 60 MHz in $CDCl_3$ and 34 °C unless stated otherwise. Resonances are singlets unless stated otherwise; d = doublet, t = triplet. *J* values ±0.5 Hz are given. [c] Recorded at 40.48 MHz in $CDCl_3$ and ambient temperature, unless stated otherwise. Resonances are singlets unless stated otherwise. dd = Doublet of doublets. Shifts, relative to 85% H_3PO_4, to low frequency are positive. [d] Proton spectrum in C_6D_6 at 90 MHz. [e] Signal obscured by other resonances. [f] Proton spectrum at 100 MHz. [g] Absent from the i.r. spectrum of the corresponding bromide but it is not clear which bands are due to ν(Pd–Cl). [h] Assigned to pyridine ring. [i] Not observed. [j] Q = $CH_3C(=NOH)C(CH_3)_3$. [k] Proton n.m.r. resonances for acac are: δ(CH) 5.20, δ(CH_3) 1.90 and 1.88 p.p.m.

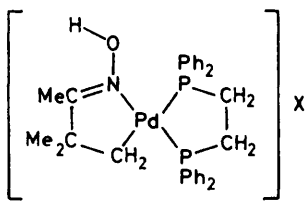
TABLE 2 (*Continued*)

Compound	I.r. ν(Pd–Cl)	I.r. ν(=CN)	^{1}H N.m.r. OCH_3	^{1}H N.m.r. $C(CH_3)_2$	^{1}H N.m.r. OCH_2CH_3
(14a)	245m, 317s	1 630	3.25	2.05, 2.25	
(14b)	245m, 315s	1 630w		2 00, 2.23	1.03 (t) J(HH) *ca.* 7
(14c)	243m, 315s	1 625	3.22		

the values of ν(Pd–Cl) (Table 2) we cannot be certain which it is. Complexes (3b) and (3c) showed more than one band in the region 220—350 cm^{-1} which were absent from (or very weak in) the i.r. spectra of the corresponding bromides (3e) and (3f) and therefore a definite assignment to ν(Pd–Cl) was not made. We favour a structure



	R	X	Q
(3a)	Me	Cl	CO
(3b)	Me	Cl	PMe_2Ph
(3c)	Me	Cl	PPh_3
(3d)	Me	Cl	py
(3e)	Me	Br	PPh_3
(3f)	Me	Br	PMe_2Ph
(3g)	Et	Cl	PPh_3
(3h)	Ph	Cl	PPh_3



(4a) X = I
(4b) X = BPh_4

for (3b) or (3c) with chlorine *trans* to methylene since the possible values of ν(Pd–Cl) (Table 2) are all lower than typical values of ν(Pd–Cl) for chlorine *trans* to nitrogen.[18,19] In the ^{1}H n.m.r. spectra the Pd–CH_2 and O–H resonances appear as a doublet with weak coupling to phosphorus-31 (confirmed by a ^{1}H-{^{31}P} experiment).

TABLE 3

Bond lengths (Å) and estimated standard deviations

(*a*) Compound (1a), see Figure 1

Pd(1)–Cl(1)	2.341(1)	Pd(2)–Cl(1)	2.343(2)
Pd(1)–Cl(2)	2.546(2)	Pd(2)–Cl(2)	2.534(2)
Pd(1)–C(4)	2.023(6)	Pd(2)–C(10)	2.009(7)
Pd(1)–N(1)	1.997(4)	Pd(2)–N(2)	1.974(4)
N(1)–C(1)	1.271(4)	N(2)–C(7)	1.300(7)
C(1)–C(3)	1.516(9)	C(7)–C(9)	1.516(8)
C(3)–C(4)	1.518(8)	C(9)–C(10)	1.511(9)
C(1)–C(2)	1.533(9)	C(7)–C(8)	1.519(10)
C(3)–C(5)	1.542(9)	C(9)–C(11)	1.555(9)
C(3)–C(6)	1.550(8)	C(9)–C(12)	1.545(9)
N(1)–O(1)	1.386(6)	N(2)–O(2)	1.412(6)
Pd · · · Pd	2.991(1)		

(*b*) Compound (6), see Figure 2

Pd–N(2)	2.027(4)	Pd–O(1)	2.109(3)
Pd–C(1)	1.991(5)	Pd–O(2)	2.024(3)
N(2)–N(1)	1.483(5)	O(1)–C(9)	1.257(5)
N(2)–C(7)	1.508(9)	O(2)–C(12)	1.276(5)
N(2)–C(8)	1.502(9)	C(9)–C(11)	1.414(7)
N(1)–C(2)	1.274(7)	C(11)–C(12)	1.397(7)
C(1)–C(2)	1.506(6)	C(9)–C(10)	1.509(7)
C(2)–C(3)	1.514(6)	C(12)–C(13)	1.508(7)
C(3)–C(4)	1.538(10)	C(3)–C(6)	1.528(8)
C(3)–C(5)	1.513(14)		

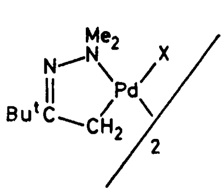
The nitrogen–palladium bonds in some *ortho*-palladated compounds can be broken by treatment with 2 mol of a tertiary phosphine to give a σ-arylpalladium complex, *e.g.* cyclopalladated azobenzene.[20] However, we find that on treatment of the mononuclear complex (3c) with a second mole of triphenylphosphine in $CDCl_3$ both the ^{31}P n.m.r. signals of (3c) and PPh_3 are observed, although slightly broadened due to rapid exchange: this exchange process also accounts for the loss of coupling to phosphorus-31 of the OH and PdCH_2 protons in the ^{1}H n.m.r. spectrum. We also studied the addition of the chelating ligand $Ph_2PCH_2CH_2PPh_2$ in ethanol. This gave the ion $[Pd\{CH_2C(CH_3)_2C(=NOH)CH_3\}(Ph_2PCH_2CH_2PPh_2)]^+$, isolated as its iodide or tetraphenylborate salts (4a) or (4b) respectively, there being no evidence of Pd–N bond breakage. The original ethanol solution formed by adding the diphosphine, $Ph_2PCH_2CH_2PPh_2$, contained this cation as the only phosphorus-containing species [^{31}P n.m.r. evidence: $\delta(P_A) = 54.1$(d), $\delta(P_B) = 35.6$(d) p.p.m., $J(P_AP_B) = 26$ Hz (using an external C_6D_6 frequency lock)].

We similarly found that the oximes of other t-butyl ketones, *viz.* ethyl t-butyl ketoxime and phenyl t-butyl ketoxime, cyclopalladated on the t-butyl group in the presence of sodium acetate to give stable crystalline (1d) and (1e) respectively (characterizing data in Tables 1 and 2, details in Experimental section). *E*-Ethyl t-butyl ketoxime was made by monomethylation (using methyl iodide) of the dilithio-derivative of *E*-methyl t-butyl ketoxime. This procedure is known to be completely regio- and stereo-specific with ketoximes.[21-23]

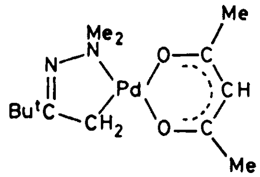
The oxime of trimethylacetaldehyde, however, when similarly treated gave an unstable very dark and intractable material as did the oximes of di-isopropyl ketone, ethyl methyl ketone, methyl isopropyl ketone, or 2-methylcyclohexanone. In the absence of sodium acetate these ketoximes all gave complexes of the well known type *trans*-$[PdCl_2L_2]$, including when L = *E*-methyl t-butyl ketoxime (for which analytical and molecular-weight data are in the Tables).

We then studied the possibility of cyclopalladating dimethylhydrazones. Treatment of methyl t-butyl *NN*-dimethylhydrazone with sodium tetrachloropalladate(II)–sodium acetate in methanol rapidly gave the cyclometallated complex (5a) as yellow needles. The ^{1}H n.m.r. spectrum showed that cyclometallation had occurred on the single methyl group and that the t-butyl group was not metallated. This strongly suggested that it was the NMe_2 nitrogen and not the N=C nitrogen which was co-ordinated to palladium. We were unable to prepare crystals suitable for *X*-ray crystallography.

However, the mononuclear acetylacetonate complex (6), prepared by treating the chloro-bridged complex with acetylacetone and sodium hydroxide solution, gave suitable crystals.



(5a) X = Cl
(5b) X = Br
(5c) X = I



(6)

The crystal structure is shown in Figure 2 and bond lengths are given in Table 3. Except for the five methyl groups of the dimethylhydrazone ligand the molecule is planar, and the differing *trans* influences of carbons and

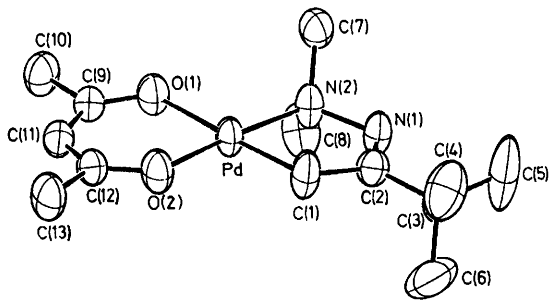
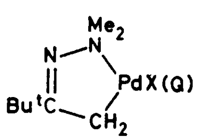
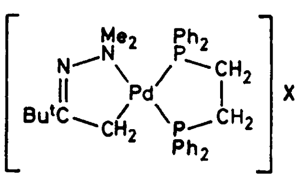


FIGURE 2 ORTEP drawing of the molecular structure of (6), 50% probability thermal ellipsoids being shown

nitrogen are reflected in the Pd–O(1) and Pd–O(2) bond lengths. The chloro-bridged binuclear complex (5a) gave the corresponding bromide (5b) or iodide (5c) on metathesis (LiBr or NaI in acetone) and underwent bridge-splitting reactions with tertiary phosphines (PPh_3 or PMe_2Ph) to give (7a) and (7b) respectively: a bromide (7c) was also prepared. The values of ν(Pd–Cl) of 285 cm^{-1} (PPh_3) or 283 cm^{-1} (PMe_2Ph) suggest that chlorine is *trans* to carbon. The mononuclear complexes (7a) or



	X	Q
(7a)	Cl	PPh_3
(7b)	Cl	PMe_2Ph
(7c)	Br	PPh_3
(7d)	Br	PMe_2Ph
(7e)	Cl	py



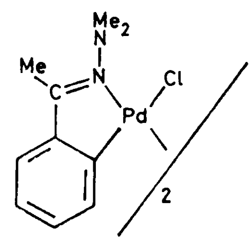
(8b) X = BPh_4

(7b) were characterized by singlet ^{31}P n.m.r. resonances and on adding a further mole of the tertiary phosphine there was no evidence of Pd–NMe_2 bond fission. With $Ph_2PCH_2CH_2PPh_2$ the binuclear complex (5a) gave only the ion $[Pd\{CH_2C(=NNMe_2)Bu^t\}(Ph_2PCH_2CH_2PPh_2)]^+$, isolated as the tetraphenylborate salt (8b).

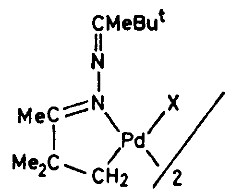
We have also attempted to cyclopalladate ethyl t-butyl ketone *NN*-dimethylhydrazone. This hydrazone was prepared by lithiating methyl t-butyl dimethylhydrazone with n-butyl-lithium in tetrahydrofuran (thf) at 0 °C followed by the addition of methyl iodide. Treatment of ethyl t-butyl ketone dimethylhydrazone with sodium tetrachloropalladate(II) and sodium acetate gave an unstable product which we were unable to isolate (possibly β-hydride elimination from the ethyl group occurs).

We also studied the dimethylhydrazones of acetaldehyde, acetone, cyclohexanone, and 4-t-butylcyclohexanone. In each case, when the hydrazone was treated with sodium tetrachloropalladate(II) and sodium acetate, decomposition occurred and we were unable to isolate products. Also in each case, with 2 mol of the dimethylhydrazone (L) per mol of palladium, in the absence of sodium acetate, mononuclear complexes of the type *trans*-$[PdCl_2L_2]$ were formed. Compounds of this type are well known and the crystal structure of *trans*-$[PdCl_2\{CH_3C(=NNMePh)CH_3\}_2]$ has been determined:[24] the hydrazone ligands are co-ordinated *via* the =N nitrogens.

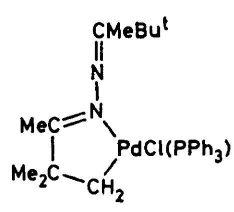
Acetophenone oxime has been shown to cyclopalladate specifically in an *ortho* position of the arene ring.[16] In view of the regiospecific and different site of cyclopalladation of methyl t-butyl ketoxime (on the Bu^t) and methyl t-butyl dimethylhydrazone (on the =CMe) we have investigated the cyclopalladation of acetophenone dimethylhydrazone. We find that cyclopalladation occurs rapidly and exclusively in the *ortho* position of the



(9)



(10a) X = Cl
(10b) X = Br
(10c) X = I



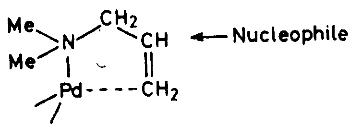
(11)

aromatic ring to give (9). We could find no evidence for cyclometallation of the methyl (=CMe) group.

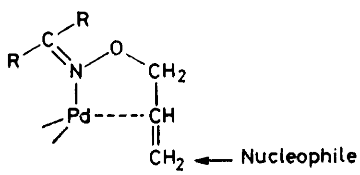
We have also investigated the palladation of methyl t-butyl ketazine, where palladation of either the methyl or the t-butyl group and/or dipalladation could occur. We find that in the presence of sodium acetate–sodium tetrachloropalladate(II) this ketazine palladates exclusively on one of the t-butyl groups to give (10a) in high yield. Characterizing data are in the Tables. The corresponding bromo- (10b) and iodo- (10c) complexes were prepared by metathesis and the bridge split by triphenylphosphine to give the mononuclear complex (11).

Thus cyclopalladation of a t-butyl group in some t-butyl ketones is readily achieved by using an oxime or an azine, whereas the dimethylhydrazone of t-butyl methyl ketone palladates exclusively and rapidly on the single methyl group. Unfortunately, as reported above, attempts to cyclopalladate less sterically hindered ketones were unsuccessful. However, there are many sterically hindered ketones, *e.g.* terpenes or steroids, where cyclopalladation of the simple nitrogen derivatives (oximes, *etc.*) might be possible.

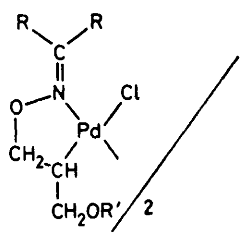
Finally, we describe some work on the cyclopalladation of acetoxime *O*-allyl ether. Allyl(dimethyl)amine in methanol is cyclopalladated and attacked by OMe on the β position of the allyl group [as in (12)] to give [Pd_2-{$Me_2NCH_2CH(OMe)CH_2$}$_2Cl_2$].[25] Analogous reactions have been shown to occur with a variety of nucleophiles and attack has been shown to be stereospecifically *trans*.[2] Two carbopalladations of this type have been



(12)



(13)



(14a) R = Me, R′ = Me
(14b) R = Me, R′ = Et
(14c) R,R = $(CH_2)_5$, R′ = Me

used in a stereospecific synthesis of prostaglandin $PGF_{2\alpha}$.[8] We thought it could be synthetically useful to carbopalladate an allylic group with concomitant nucleophilic attack on the terminal (*i.e.* γ) position as in (13). We therefore studied the possibility of such an attack on the *O*-allyl ether of acetoxime. Treatment of this *O*-allyl ether with sodium tetrachloropalladate(II) in methanol (or ethanol) gave binuclear complexes which we formulate as (14a) or (14b) respectively. They were obtained as pale yellow crystalline solids soluble in common organic solvents but they decomposed gradually on solution at room temperature to give palladium metal. The strong band at 1 645 cm^{-1} in the i.r. absorption spectrum of acetoxime *O*-allyl ether due to ν(C=C) is absent in the i.r. spectra of the complexes, whilst the much weaker band due to ν(C=N) is still present (at 1 630 cm^{-1}). The ^1H n.m.r. spectra (Table 2) showed the absence of olefinic protons but the absorption due to the $-CH_2CHCH_2-O$ system was too complex to assign (five non-equivalent hydrogens). Many nitrogen donors have been cyclopalladated previously and all have given a five-membered palladocycle ring. We therefore think it extremely likely that OMe(OEt) attack occurs on the γ rather than the β position (to give a six-membered palladocycle ring). We have not extended this reaction to other nucleophiles but it should be possible to do so. It seems likely that nucleophilic attack will be specifically *trans* and that the reaction could be useful in synthesis. The *O*-allyl ether of cyclohexanone oxime was similarly cyclopalladated with OMe attack to give (14c). Acetoxime and cyclohexanone oxime *O*-allyl ethers were prepared by a literature method.[26]

EXPERIMENTAL

The general procedures and spectroscopic techniques were the same as those described in other recent papers from this laboratory.[27]

[Pd_2{$CH_2C(CH_3)_2C(=NOH)CH_3$}$_2Cl_2$] (1a).—A solution of *E*-methyl t-butyl ketoxime (0.637 g, 5.5 mmol), sodium tetrachloropalladate(II) (2.02 g, 5.5 mmol), and sodium acetate (0.462 g, 5.6 mmol) in methanol (20 cm^3) was set aside at room temperature for 3 d. The solvent was removed under reduced pressure and the residue was extracted with dichloromethane (4 × 25 cm^3). Evaporation of the extract under reduced pressure gave a solid from which the required product (0.995 g, 1.94 mmol, 71%), m.p. 156—160 °C, was obtained as orange needles on recrystallization from methanol.

(1b).—A large excess (*ca.* 20-fold) of lithium bromide was added to a solution of the chloride (1a) (0.16 g, 0.313 mmol) in acetone (15 cm^3). The yellow solution was set aside for 20 min at room temperature. The acetone was removed under reduced pressure and water (20 cm^3) was added. A yellow solid was isolated, dried, redissolved in acetone (15 cm^3), and the above procedure repeated. Recrystallization from ethanol gave the product as yellow needles (0.124 g, 0.206 mmol, 66%), m.p. 193—195 °C (with decomposition).

(1c).—A solution of the chloride (1a) (0.154 g, 0.30 mmol) in acetone (15 cm^3) was treated with a large excess (*ca.* 20-fold) of sodium iodide. The solution was set aside for 20 min, the solvent was evaporated under reduced pressure, and water (20 cm^3) was added. A yellow solid was filtered off and recrystallized from dichloromethane–methanol to give the iodide (1c) as yellow needles (0.168 g, 0.242 mmol, 80%), m.p. 185—192 °C (with decomposition).

E-*Ethyl t-Butyl Ketoxime*.—A solution of *E*-methyl t-butyl ketoxime (3.55 g, 0.30 mmol) in dry thf (50 cm^3) was treated dropwise with n-butyl-lithium (0.12 mol) in n-hexane (48 cm^3) to give a yellow solution. The resultant yellow solution was cooled to 0 °C and stirred for 1 h after which a solution of methyl iodide (9.4 g, 0.066 mol) in dry thf (50 cm^3) was added dropwise. The resultant solution was stirred for 1.5 h allowing it to come to room temperature. The solution was evaporated and the product isolated with diethyl ether. It formed colourless prisms, m.p. 78—82 °C, from methanol. Yield 2.52 g (0.20 mol, 66%).

(1d).—A solution of *E*-ethyl t-butyl ketoxime (0.129 g, 1.00 mmol), Na[$PdCl_4$] (0.339 g, 1.00 mmol), and sodium acetate (0.082 g, 1.00 mmol) in methanol (6 cm^3) was put aside at *ca.* 20 °C for 4 d. The solvent was evaporated under reduced pressure and the required product isolated with light petroleum (b.p. 60—80 °C) as pale yellow needles, m.p. 125—128 °C. Yield 0.12 g (0.225 mmol, 45%).

(1e).—A solution of phenyl t-butyl ketoxime (0.354 g, 2.00 mmol), $Na[PdCl_4]$ (0.733 g, 2.00 mmol), and sodium acetate (0.165 g, 2.00 mmol) in methanol (14 cm^3) was set aside at room temperature for 4 d. Some palladium was deposited along with a pale yellow solid. The solids were extracted with dichloromethane and methanol added to the extract to give the required product as yellow needles, m.p. 187—192 °C (decomposition). Yield 0.339 g (0.54 mmol, 54%).

The Acetate (2).—The chloro-complex (1a) (0.152 g, 0.296 mmol) was heated in boiling acetic anhydride (3 cm^3) for *ca.* 10 s to give a dark orange solution, which was then set aside for 3 d in air. The resultant precipitate was recrystallized from ethanol to give the required product as yellow needles, m.p. 195—197 °C (with decomposition). Yield 0.122 g (0.206 mmol, 70%).

The Carbonyl Complex (3a).—A suspension of the bridged chloro-complex (1a) (0.253 g, 0.493 mmol) in methanol (10 cm^3) was treated with carbon monoxide for *ca.* 5 min. Addition of water (25 cm^3) to the resulting colourless solution gave (3a) as white microcrystals (0.136 g, 0.479 mmol, 49%). These decomposed above 45 °C to give back the yellow bridged chloro-complex (1a), and the complex was not obtained analytically pure (see Discussion).

(3b).—Dimethylphenylphosphine (0.17 cm^3, 1.2 mmol) was syringed into a suspension of the bridged chloro-complex (1a) (0.30 g, 0.59 mmol) in methanol (8 cm^3). The required product was isolated from the resultant yellow solution by evaporation and recrystallization of the residue from light petroleum (b.p. 60—100 °C) as white needles, m.p. 103—105 °C (with decomposition). Yield 0.30 g (0.76 mmol, 65%).

(3c).—A mixture of triphenylphosphine (0.259 g, 0.988 mmol) and the chloro-complex (1a) (0.251 g, 0.490 mmol) was heated under reflux in methanol (8 cm^3) for 10 min. The white solid that formed was recrystallized from ethanol to give the required complex (3c) as cream plates (0.406 g, 0.783 mmol, 80%), m.p. 187—189 °C. Complexes (3g) and (3h) were prepared similarly as white prisms, m.p. 213—216 and 188—191 °C (both with decomposition), respectively.

(3d).—Pyridine (0.035 g, 0.447 mmol) was added to a solution of the chloro-complex (1a) (0.108 g, 0.212 mmol) in chloroform (3 cm^3). The colourless solution was set aside for 5 min, light petroleum (b.p. 60—80 °C) (6 cm^3) was added, and the solution was allowed to evaporate to *ca.* 4 cm^3. The solid that separated gave the required complex (3d) as colourless prisms (0.122 g, 0.363 mmol, 86%), m.p. 133—140 °C, on recrystallization from chloroform–light petroleum (b.p. 60—80 °C).

(3e).—A solution of the chloro-complex (3c) (0.131 g, 0.253 mmol) in acetone (10 cm^3) was treated with a large excess (*ca.* 20-fold) of lithium bromide to give a yellow solution which was set aside for 1 h. The acetone was then removed under reduced pressure and water (20 cm^3) was added. A yellow solid was isolated, dried, redissolved in acetone (10 cm^3), and the above process repeated. The product was isolated as pale yellow prisms (0.071 g, 0.125 mmol, 50%), m.p. 172—175 °C, from ethanol. Complex (3f) was prepared in a similar manner from (3b), as white microcrystals (40% yield), m.p. 110—112 °C, from light petroleum (b.p. 80—100 °C).

The Salts (4a) *and* (4b).—A mixture of the bridged chloro-complex (1a) (0.27 g, 0.53 mmol) and 1,2-bis(diphenylphosphino)ethane (0.425 g, 1.06 mmol) in ethanol (8 cm^3) was heated to give a clear colourless solution. The $^{31}P-^{1}H$ n.m.r. spectrum was recorded (see Discussion) and the solution was then divided into two portions in the ratio 3 : 1. To the larger portion was added sodium iodide (0.24 g, 1.6 mmol) in ethanol (4 cm^3) followed by water (10 cm^3), dropwise. This gave the iodide (4a) as white microprisms, m.p. 189—192 °C (with decomposition). Yield 0.49 g (*ca.* 80%). To the smaller portion was added a solution of sodium tetraphenylborate (0.185 g, 0.54 mmol) in ethanol (5 cm^3). The resultant white precipitate was recrystallized from dichloromethane–light petroleum (b.p. 60—80 °C) to give (4b) as white prisms, m.p. 96—100 °C. Yield 0.23 g (0.24 mmol, *ca.* 90%).

$[Pd\{CH_3C(=NOH)C(CH_3)_3\}_2Cl_2]$.—A mixture of $Na_2[PdCl_4]$ (0.487 g, 1.54 mmol) and methyl t-butyl ketoxime (0.389 g, 3.38 mmol) in methanol (3 cm^3) was set aside at room temperature for 1 d. The solvent was evaporated under reduced pressure and the residue was recrystallized from dichloromethane–light petroleum (b.p. 60—80 °C) to give the product as yellow needles (0.256 g, 0.63 mmol, 41%), m.p. 150—155 °C (with decomposition).

$[Pd_2\{CH_2C(=NNMe_2)C(CH_3)_3\}_2Cl_2]$ (5a).—Methyl t-butyl ketone *NN*-dimethyl hydrazone (0.63 g, 4.43 mmol) and sodium acetate (0.332 g, 4.05 mmol) were added to a solution of $Na_2[PdCl_4]$ (1.37 g, 4.03 mmol) in methanol (12 cm^3). A precipitate formed after *ca.* 5 min but the mixture was set aside for 24 h. The solvent was then evaporated under reduced pressure and the residue extracted with dichloromethane. Isolation gave the required product (5a) as yellow needles (0.95 g, 1.68 mmol, 83%), m.p. 208—211 °C (with decomposition), from dichloromethane–methanol.

The Bridged Bromide (5b).—Treatment of a suspension of the corresponding chloride (5a) (0.301 g, 0.532 mmol) in acetone (10 cm^3) with a large excess (*ca.* 10-fold) of lithium bromide gave a yellow solution, which was set aside for 30 min at room temperature. The acetone was removed under reduced pressure and water (20 cm^3) added. A yellow solid was isolated, dried, redissolved in acetone (10 cm^3), and the above procedure repeated. The required product formed yellow needles (0.267 g, 0.408 mmol, 77%), m.p. 188—193 °C (with decomposition), from dichloromethane–light petroleum (b.p. 60—80 °C).

The bridged iodide (5c) was prepared similarly from the chloride using sodium iodide. It formed yellow needles, m.p. 203—205 °C (with decomposition) from ethanol. Yield 79%.

$[Pd\{CH_2C(=NNMe_2)C(CH_3)_3\}(acac)]$ (6).—A mixture of the bridged chloride complex (5a) (0.178 g, 0.315 mmol), acetylacetone (0.069 g, 0.693 mmol), and sodium hydroxide (0.027 g, 0.683 mmol) in methanol (6 cm^3) was set aside at room temperature for 18 h. The solid which separated out was recrystallized from methanol to give the product as colourless needles (0.131 g, 0.378 mmol, 60%), m.p. 119—123 °C.

$[Pd\{CH_2C(=NNMe_2)C(CH_3)_3\}Cl(py)]$ (7e).—Pyridine (0.031g, 0.40 mmol) was added to a suspension of the bridged chloride complex (5a) (0.101 g, 0.179 mmol) in methanol (4 cm^3). The solution was set aside for 12 h, evaporated to dryness under reduced pressure, and the residue recrystallized from dichloromethane–light petroleum (b.p. 60—80 °C) to give the product (7e) as colourless prisms (0.11 g, 0.305 mmol, 85%). It sublimes above 130 °C with m.p. 221—224 °C (with decomposition).

Complex (7a) was prepared in a similar manner as colourless needles, 76% yield, m.p. 212—217 °C, as was (7b) as white prisms, 63% yield, m.p. 160—163 °C.

(7c).—A solution of the bridged bromide complex (5b) (0.126 g, 0.193 mmol) and triphenylphosphine (0.101 g, 0.386 mmol) in dichloromethane (5 cm^3) was set aside at room temperature for 5 min. The solvent was then removed under reduced pressure and the residue was recrystallized to give the product (7c) as white needles (0.18 g, 0.305 mmol, 79%), m.p. 226—230 °C (with decomposition), from dichloromethane–light petroleum (b.p. 60—80 °C). Complex (7d) was prepared in a similar manner as yellow plates, m.p. 143—148 °C. Yield 81%.

(8b).—A mixture of 1,2-bis(diphenylphosphino)ethane (0.141 g, 0.354 mmol) and the bridged chloride complex (5a) (0.10 g, 0.177 mmol) was heated in ethanol (3 cm^3) to give a colourless solution. Addition of Na[BPh_4] (0.243 g, 0.711 mmol) gave an immediate precipitate which was filtered off, washed with water (10 cm^3), and then ethanol (10 cm^3), to give the product as white microcrystals (0.315 g, 0.326 mmol, 92%), m.p. 143—145 °C.

[$Pd_2\{C_6H_4C(=NNMe_2)CH_3\}_2Cl_2$] (9).—A solution of hydrated Na_2[$PdCl_4$] (0.366 g, 1.00 mmol), sodium acetate (0.082 g, 1.00 mmol), and acetophenone dimethylhydrazone (0.162 g, 1.00 mmol) in methanol (7 cm^3) was set aside at room temperature for 18 h. The crystalline product was washed with water and recrystallized from methanol. It formed yellow prisms (0.302 g, 0.50 mmol, 100%), m.p. 188—190 °C (with decomposition).

[$Pd_2\{CH_2C(CH_3)_2C(=NN=CMeBu^t)CH_3\}_2Cl_2$] (10a).—A mixture of methyl t-butyl ketazine (0.228 g, 1.16 mmol), hydrated Na_2[$PdCl_4$] (0.36 g, 1.06 mmol), and sodium acetate (0.096 g, 1.17 mmol) in methanol (10 cm^3) was set aside at room temperature for 24 h. The resulting precipitate was recrystallized from dichloromethane–light petroleum (b.p. 60—80 °C) to give the required product as yellow prisms (0.268 g, 0.396 mmol, 75%), m.p. >300 °C.

(10b).—Treatment of a suspension of the chloride-bridged complex (10a) (0.25 g, 0.371 mmol) in acetone (8 cm^3) with a large excess (*ca.* 20-fold) of lithium bromide gave an orange solution which was set aside at room temperature for 1 h. The solvent was removed under reduced pressure and water (20 cm^3) was added. A solid was isolated, dried, redissolved in acetone (8 cm^3), and the above procedure repeated. The product was obtained as orange prisms (0.229 g, 0.30 mmol, 81%), m.p. 274—276 °C (with decomposition), on recrystallization from dichloromethane–light petroleum (b.p. 60—80 °C). The iodide-bridged complex (10c) was (prepared similarly as red microcrystals, m.p. 260—263 °C (with decomposition). Yield 73%.

[$Pd_2\{CH(CH_2OCH_3)CH_2ON=C(CH_3)_2\}_2Cl_2$] (14a).—Acetoxime *O*-allyl ether (0.233 g, 2.065 mmol) and sodium acetate (0.154 g, 1.88 mmol) were added to a solution of hydrated Na_2[$PdCl_4$] (0.638 g, 1.88 mmol) in methanol (5 cm^3). The yellow solution was cooled at 0 °C for 2.5 h. The precipitate was filtered off, washed with water (10 cm^3), and recrystallized from dichloromethane–light petroleum (b.p. 40—60 °C) as yellow microcrystals (0.262 g, 0.459 mmol, 49%), m.p. 110—112 °C (with decomposition).

Complex (14b) was prepared similarly as pale yellow microcrystals, 35% yield, m.p. 91—93 °C (with decomposition), with ethanol as the solvent, as was (14c) as pale yellow microcrystals, 65% yield, m.p. 100—102 °C (with decomposition), from cyclohexanone oxime *O*-allyl ether, with methanol as the solvent.

Crystal Data.—(1a), $C_{12}H_{24}Cl_2N_2O_2Pd_2$, $M = 512.0$, Monoclinic, $a = 7.312(1)$, $b = 8.539(2)$, $c = 28.478(4)$ Å, $\beta = 91.74(1)°$, $U = 1\,777.2(5)$ Å^3, $Z = 4$, $D_c = 1.913$ g cm^{-3}, $F(000) = 1\,008$, space group $P2_1/c$, Mo-K_α radiation (graphite monochromated), $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 23.05 cm^{-1}.

(6) $C_{13}H_{24}N_2O_2Pd$, $M = 346.7$, Triclinic, $a = 9.573(3)$, $b = 10.714(3)$, $c = 8.983(2)$ Å, $\alpha = 94.41(2)$, $\beta = 113.76(2)$, $\gamma = 104.65(2)°$, $U = 799.0(3)$ Å^3, $Z = 2$, $D_c = 1.441$ g cm^{-3}, $F(000) = 448$, space group $P\bar{1}$, μ(Mo-K_α) = 11.43 cm^{-1}.

Structure Determination.—For each compound, cell dimensions were determined by least-squares treatment of the setting angles for 15 reflections having $35 < 2\theta < 40°$. Intensities of all independent reflections with $5 < 2\theta < 50°$ were measured in the θ—2θ scan mode, using scan speeds varying between 2 and 29° min^{-1}. The structure analyses used the 2 698 reflections having $I > 3\sigma(I)$ (with another 453 rejected) for (1a) and 2 543 having $I > 3\sigma(I)$ (with another 292 rejected) for (6). After correction for Lorentz, polarization, and transmission factors, and solution of the structures by Patterson and electron-density syntheses, the structures were refined by least squares with, in the final stages, anisotropic temperature factors for all non-hydrogen atoms. Least-squares weights were derived from the modified variances $\sigma^2(I) = \sigma_c^2(I) + (0.03I)^2$, where σ_c^2 is the variance from counting statistics. Atomic scattering factors were calculated from the analytical approximation

TABLE 4

Atomic co-ordinates and estimated standard deviations

(*a*) Compound (1a)

Pd(1)	0.213 70(6)	0.274 14(5)	0.068 40(1)
Pd(2)	0.225 27(5)	0.074 29(5)	0.154 70(1)
Cl(1)	0.456 79(19)	0.224 58(18)	0.121 72(5)
Cl(2)	−0.010 16(21)	0.283 95(18)	0.135 09(5)
C(1)	0.054 2(8)	0.281 3(6)	−0.024 00(19)
C(2)	−0.093 4(10)	0.293 5(9)	−0.063 2(2)
C(3)	0.252 0(8)	0.239 7(6)	−0.032 4(2)
C(4)	0.365 8(8)	0.289 8(7)	0.010 4(2)
C(5)	0.320 0(11)	0.323 4(9)	−0.076 6(2)
C(6)	0.256 8(11)	0.059 7(7)	−0.039 5(3)
C(7)	0.087 3(8)	−0.202 9(7)	0.199 0(2)
C(8)	−0.051 6(10)	−0.318 4(9)	0.217 3(3)
C(9)	0.292 7(8)	−0.226 4(7)	0.202 6(2)
C(10)	0.384 8(9)	−0.110 8(8)	0.170 8(3)
C(11)	0.340 8(11)	−0.394 8(8)	0.186 2(3)
C(12)	0.353 1(11)	−0.200 6(12)	0.254 4(2)
N(1)	0.015 8(6)	0.297 1(5)	0.019 0(2)
N(2)	0.041 0(6)	−0.070 4(5)	0.179 5(2)
O(1)	−0.164 9(5)	0.326 3(5)	0.029 5(2)
O(2)	−0.148 5(5)	−0.038 7(5)	0.176 5(2)

(*b*) Compound (6)

Pd(1)	0.332 86(4)	0.591 36(3)	0.547 29(4)
C(1)	0.266 3(7)	0.395 4(5)	0.504 6(6)
C(2)	0.136 8(5)	0.342 2(5)	0.329 5(5)
C(3)	0.045 1(6)	0.196 5(5)	0.271 1(6)
C(4)	0.161 4(8)	0.114 9(6)	0.328 1(10)
C(5)	−0.069 1(10)	0.164 0(8)	0.350 2(13)
C(6)	−0.042 6(11)	0.155 0(7)	0.082 0(9)
C(7)	0.064 0(7)	0.626 0(6)	0.263 5(8)
C(8)	0.286 9(7)	0.602 7(5)	0.207 0(7)
C(9)	0.473 4(5)	0.874 6(5)	0.717 0(6)
C(10)	0.498 4(7)	1.019 6(5)	0.718 0(7)
C(11)	0.544 2(6)	0.837 7(5)	0.871 4(6)
C(12)	0.542 9(5)	0.710 9(5)	0.898 5(5)
C(13)	0.637 7(7)	0.695 8(6)	1.072 9(7)
N(1)	0.099 3(5)	0.416 3(4)	0.225 2(5)
N(2)	0.190 1(5)	0.557 3(4)	0.300 2(5)
O(1)	0.394 0(4)	0.798 1(3)	0.577 4(4)
O(2)	0.470 5(4)	0.603 2(3)	0.791 0(4)

and coefficients given in ref. 28. The final values of R and R' were 0.032 and 0.049 for (1a), 0.036 and 0.054 for (1b). Hydrogen atoms appeared in final difference syntheses, but were not included in the structure-factor calculations. The atomic co-ordinates and estimated standard deviations are given in Table 4. The vibrational parameters and the observed and calculated structure factors are in Supplementary Publication No. SUP 22810 (37 pp.).*

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