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FUNCTIONALISATION OF UNACTIVATED METHYL GROUPS THROUGH CYCLOPALLADATION REACTIONS

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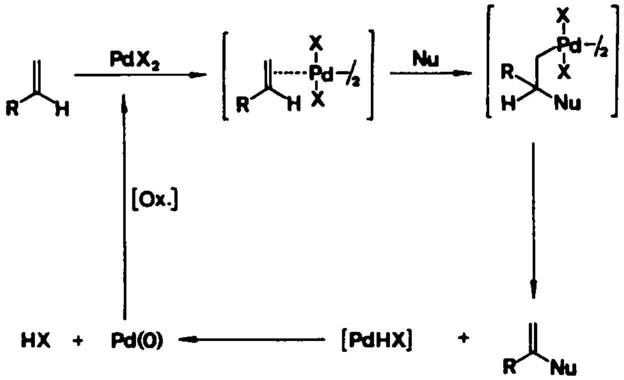
Abstract - The transformation of the organopalladium compound (3) into the corresponding deuteriated, chlorinated, or oxidized derivatives (7), (8), or (9), (11), and (12) respectively, is described. The palladation of compound (9) takes place regioselectively leading to the palladated system (13), which is transformed into the difunctionalised oximes (15) and (16). The palladation of E-2,2-dimethyl and 2,2,6,6-tetramethyl-cyclohexanone oxime leads to the corresponding organopalladium compounds (17) and (27), which through deuteriation or oxidation affords the expected products (21) and (31), or (22), (23), (24), and (32), respectively. The second palladation of the compound (22) takes place on the remaining methyl group yielding the organopalladium derivative (26). Finally, E-lupanone oxime is palladated selectively in the 23-position leading to the organopalladium compound (38); the transformation of this compound into its 23-deuterio and 23-acetoxy- derivatives (41) and (42), respectively is also described. The stereochemistry in the palladation of lupanone oxime is deduced from NOE studies at 500 MHz.

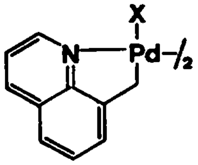
Introduction

σ-Organopalladium compounds are very versatile in organic syntheses and in catalytic processes,[2] one of the most important reaction being the palladium(II) assisted nucleophilic attack on olefins. If the σ-organopalladium intermediate bears a hydrogen atom at the β-position with respect to the palladium atom it decomposes through a 'PdHX' β-elimination (Scheme).

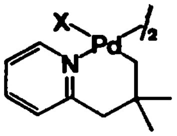


Scheme

However, σ-organopalladium compounds lacking β-hydrogen atoms are usually quite stable species, for example the products (1),[3] (2),[4] or (3).[5]



(1)



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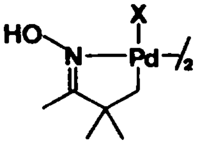


(3)

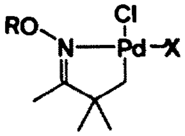
We were interested in the possible applications of organopalladium compounds derived from substituted cyclic oximes of the type (3) in order to functionallise unactivated methyl groups.[6,7]

RESULTS AND DISCUSSION

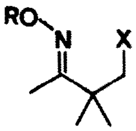
Functionalisation of the Organopalladium Compound (3). From the previous work of Shaw *et al*[5] the reaction of *E*-pinacolone oxime with disodium tetrachloropalladate-sodium acetate in ethanol led to the dimeric organopalladium compound (3), which could be transformed into the corresponding monomeric complexes (4) and (5) by treatment with pyridine or triphenylphosphine, respectively. When the dimer (3) was treated successively with acetic anhydride and pyridine the new O-acetylated pyridine complex (6) was obtained in 90% yield. The stereochemistry in (3) was deduced by X-ray analysis and in the monomeric complexes (4) and (5) by i.r. and ^{1}H n.m.r. data.[5]

The reactivity of the compound (3) toward different reagents was studied in order to functionalise the C-Pd bond. Thus, the reduction of compound (3) with sodium cyanoborodeuteride in methanol-tetrahydrofuran solution[8] afforded the deuteriated product (7) in 41% yield. The chlorination of the same starting organopalladium compound (3) with chlorine in carbon tetrachloride followed by reduction with sodium cyanoborohydride[9] led to the expected palladium-chlorine exchange and product (8) was isolated (64% overall yield). When the chlorination was carried out in other solvents, e.g. water-dioxan or dichloromethane, only decomposition products were observed.

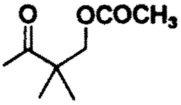
The oxidation of compound (3) with *N*-bromosuccinimide[10], *m*-chloroperbenzoic acid,[11] or lead tetraacetate[10] afforded mixtures of oxidized and halogenated products.[7] However, when oxidation was performed on the pyridine complex (4) oxidation proceeded smoothly with lead tetraacetate and compound (9) was isolated, after reduction with sodium borohydride[9], in *ca*. quantitative yield. Hydrolysis of the acetoxyoxime (9) with potassium hydroxide-ethanol led to the corresponding hydroxy derivative (10) in 35% yield.



(3) R=H, X=½
(4) R=H, X=Py
(5) R=H, X=PPh$_3$
(6) R=CH$_3$CO, X=Py



(7) R=H, X=D
(8) R=H, X=Cl
(9) R=H, X=OCOCH$_3$
(10) R=H, X=OH
(11) R=CH$_3$CO, X=OCOCH$_3$



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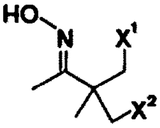
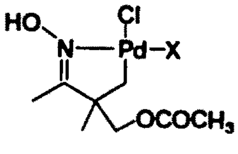


(15) X^1=D, X^2=OCOCH$_3$
(16) X^1=X^2=OCOCH$_3$



(13) X=½
(14) X=PPh$_3$

The oxidation can be also carried out on the protected O-acetylated pyridine complex (6). Thus, when compound (3) was successively treated with acetic anhydride, pyridine, and lead tetraacetate the expected O-acetylated acetoxy oxime (11) was isolated after reduction with sodium borohydride[9] in overall 83% yield.

Since the lead tetraacetate oxidation of oximes[12] gives the corresponding carbonyl compounds, when they are not too hindered,[13] we attempted the simultaneous oxidation of the C-Pd and C=NOH bonds with lead tetraacetate. Thus, when the previously described oxidation was carried out in the presence of two mol of oxidant per mol of the in situ generated pyridine complex (4) the acetylated hydroxy ketone (12) was obtained in 64% overall yield.

We also attempted carbonylation of compound (3) under different reaction conditions. When the reaction was carried out in refluxing toluene the formation of the corresponding unstable CO complex[5] was observed. The same reaction carried out in refluxing ethanol led to palladium(0) and a product which appears to be the corresponding oxidized dimeric oxime.[14] The exact structure of this product has not been determined but, in any case, the expected CO insertion was not observed.

Finally, we attempted the transmetallation Pd-Li to usefully activate the C-Pd bond. However, the transmetallation with butyl lithium, lithium metal, or lithium naphthalenide and subsequent treatment with electrophiles (methyl iodide or benzaldehyde) failed, yielding in our hands only decomposition products.

A two stage palladation via compound (9) was carried out to establish the regiochemistry of the second metallation since the palladium could be bonded to a methyl or a methylene carbon atom. We found that palladation of (9) takes place exclusively on one of the remaining methyl groups yielding the dimeric organopalladium compound (13) in 83% yield, which was transformed into the phosphine complex (14) in 71% yield. The organopalladium compound (13) was transformed into the corresponding deuterio or acetoxy derivatives (15) amd (16) by the previously described reduction or oxidation sequences respectively in 98% and 86% yield.

Preparation and Reactivity of Palladated 2,2-Dimethyl- and 2,2,6,6-Tetrametyl- Cyclohexanone Oximes. The palladation of E-2,2-dimethylcyclohexanone oxime[15] led to the corresponding dimeric organopalladium compound (17) in 85% yield. This substance was transformed into the complexes (18) and (19) by treatment with pyridine or triphenylphosphine in 95% and 99% yield, respectively. The structure of complex (18) was determined by X-ray crystallography. Acetylation prior to formation of the pyridine complex afforded the O-acetylated derivative (20) in 68% overall yield.

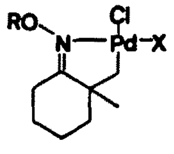
Reduction of (17) with sodium cyanoborodeuteride led to Pd-D exchange and (21) was isolated in 89% yield. Oxidation with lead tetraacetate yielded, depending on the reaction stoichiometry, products (22) or (24). Thus, using one mol of oxidant per mol of the in situ generated pyridine complex (18) the oxidation, followed by reduction with sodium borohydride,[9] led to acetoxyoxime (22) in 96% yield. When two mol of lead tetraacetate per mol of the in situ generated complex (18) was employed the corresponding acetoxyketone (24) was isolated in 58% yield. In this last case the reaction conditions must be controlled since if the reflux time was longer than two hours some of the corresponding α,β-unsaturated ketone (25) was obtained as by-product. If some over oxidation to (25) occurs the mixture can be easily transformed into (24) by catalytic hydrogenation with palladium on charcoal.

The oxidation of O-acetylated pyridine complex (20) with lead tetraacetate (1:1 molar ratio) followed by reduction with sodium borohydride[9] led to the expected product (23) in 79% yield.

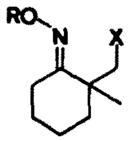
The chlorination of compound (17) with chlorine in carbon tetrachloride led to a mixture of chlorinated compounds from Pd-Cl exchange and also from α-chlorination of the oxime.

We have studied the regiochemistry of the second palladation on compound (22) and found that this process afforded exclusively the product with the palladium atom bonded to the remaining methyl group[16] isolated as the corresponding triphenylphosphine complex (26) (82% yield).

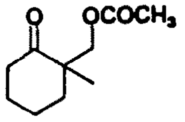
Next we studied the palladation and subseqeunt reactions of a very hindered ketone oxime, 2,2,6,6-tetramethylcyclohexanone oxime.[17] The palladation of this oxime under the standard conditions afforded the corresponding organopalladium dimer (27) in 86% yield, which upon treatment



(17) $R=H, X=\frac{1}{2}$
(18) $R=H, X=Py$
(19) $R=H, X=PPh_3$
(20) $R=CH_3CO, X=Py$



(21) $R=H, X=D$
(22) $R=H, X=OCOCH_3$
(23) $R=CH_3CO, X=OCOCH_3$



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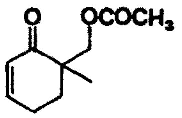

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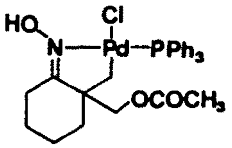

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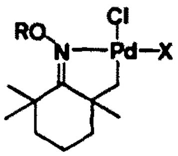
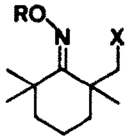


(27) $R=H, X=\frac{1}{2}$
(28) $R=H, X=Py$
(29) $R=H, X=PPh_3$
(30) $R=CH_3CO, X=Py$



(31) $R=H, X=D$
(32) $R=CH_3CO, X=OCOCH_3$

with pyridine or triphenylphospine led to the corresponding complexes (28) and (29), respectively in *ca.* 100% and 90% yield. Acetylation of (27) with acetic anhydride and subsequent treatment with pyridine yielded the *O*-acetylated pyridine complex (30) (91% yield).

The deuteriation of compound (27) led to the expected product (31) (64% yield). However, oxidation of (27) through the *in situ* generated pyridine complex (28) afforded a mixture of both *Z*- and *E*-acetoxy oximes in good yield (94%, *ca.* 1:1 molar ratio) arising from isomerisation of the oxime group under the reaction conditions. To avoid this problem we protected first the oxime group of (29) by acetylation. Then, the oxidation of the pyridine complex (30) with lead tetra-acetate followed by reduction with sodium borohydride led to the expected product (32) (83% yield).

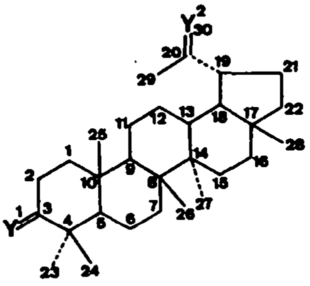
Attempts at chlorination of (27) with chlorine in carbon tetrachloride yielded only an intractable mixture of reaction products.

Finally, we studied the palladation of oximes derived from 2-methylcyclohexanone,[18] 2,2-dimethylcyclopentanone,[19] (-)-carvone,[20] (-)-fenchone,[21] and (+)-camphor.[22] These reactions were unsuccessful and either the corresponding oxime complexes or intractable mixtures were obtained.[5,23]

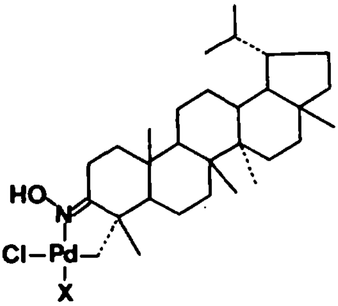
Preparation and Reactivity of Palladated Lupanone Oxime. *E*-Lupanone oxime (37) was prepared from lupenyl acetate (33),[24] which was successively hydrogenated to lupanyl acetate (34) (*ca.* 100% yield),[25] hydrolyzed to lupanol (35) (86% yield),[25] oxidized[26] to lupanone (36) (86% yield),[25] and finally treated with hydroxylamine hydrochloride (89%).

The palladation of E-lupanone oxime (37) by the above described method led to the expected dimeric organopalladium compound (38) in 76% yield. That the palladation took place at the equatorial methyl group (23-CH$_3$) was confirmed by NOE studies at 500MHz.[27] The dimeric compound (38) was transformed into the corresponding monomeric complexes (39) and (40) by treatment with pyridine or triphenylphosphine, respectively, in 97% and *ca*. 100% yield.

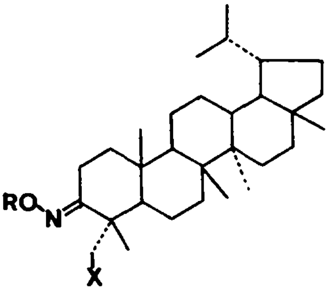
The reduction of compound (38) with sodium cyanoborohydride led to the corresponding 23-deuteriolupanone oxime (41) in 91% yield. Oxidation of (38) with lead tetraacetate through the *in situ* generated pyridine complex (39) was unsuccessful, but when the same reaction was carried out with the *in situ* formed O-acetyl pyridine complex of (38) successive oxidation with lead tetraacetate and reduction with sodium borohydride led to the expected 23-acetoxy derivative (42) in 90% yield. The stereochemistry of (41) and (42) was based on that determined of the organopalladium dimer (38). The ^{1}H, ^{2}H, and ^{13}C n.m.r. data for the lupanone derivatives were also in agreement with the assigned stereochemistry.



(33) Y^1=H, β-OCOCH$_3$; Y^2=CH$_2$
(34) Y^1=H, β-OCOCH$_3$; Y^2=H,CH$_3$
(35) Y^1=H, β-OH; Y^2=H,CH$_3$
(36) Y^1=O; Y^2=H,CH$_3$
(37) Y^1=E-NOH; Y^2=H,CH$_3$



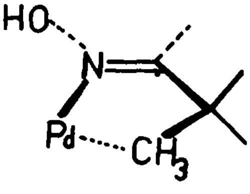
(38) X=½
(39) X=Py
(40) X=PPh$_3$



(41) R=H, X=D
(42) R=CH$_3$CO, X=OCOCH$_3$

Stereoelectronic Considerations. The exclusive functionalisation of the equatorial methyl group (23-CH$_3$) in lupanone oxime, the course of the two-stage palladation sequence on 2,2-dimethylcyclohexanone oxime and the course of the two-stage palladation sequence on pinacolone oxime deserve comment. All of these results can be explained by the operation of two effects:-

(1) Cyclopalladation is facilitated by a coplanar arrangement of the oxime and the "target" methyl group. This is perhaps unexceptional since it is the geometry giving closest approach between the oxime-coordinated palladium and the methyl hydrogens; as in (43).



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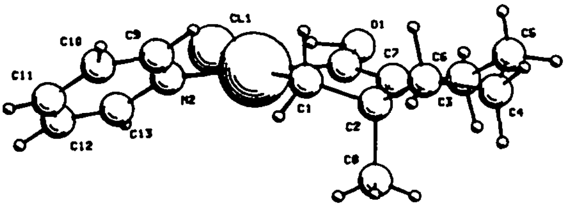
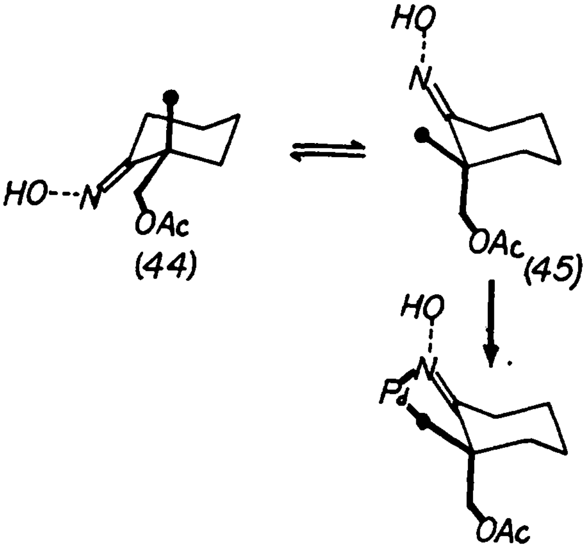


Figure 1

This geometry is achieved by the equatorial methyl group in a 2-methyl substituted cyclohexanone oxime. This requirement also explains why cyclopentanone oximes were not suitable substrates for this reaction, vide supra. The crystal structure of the monomeric pyridine complex (18), fig.1, shows the expected near-coplanarity of the oxime double bond and the palladium bearing methyl group, confirming in the product the general validity of this effect.

(2) The operation of $A^{(1,3)}$ strain[14] in 2-disubstituted cyclohexanone oximes, and perhaps even in the case of pinacolone oximes, will result in a preference for the larger of the 2-substituents being axial. Thus compound (22), the substrate for a second stage of



(44) (45)

cyclopalladation, will prefer conformation (45) over (44). Consequently, the second functionalisation will occur, from consideration (1) above, at the unfunctionalised methyl group, as was indeed observed.

EXPERIMENTAL

General.- M.p.s are uncorrected and were measured on a Buchi-Tottoli capillary melting-point apparatus. I.r. spectra were determined with a Perkin-Elmer 257 spectrometer. ^1H n.m.r. spectra were recorded in a Bruker WH 300; ^2H, ^{13}C, and ^{31}P n.m.r. spectra were measured in a Bruker AM

250. The NOE studies were carried out in a Bruker AM 500 instrument.[27] All ^{1}H, ^{13}C, and ^{31}P n.m.r. were performed in deuteriochloroform; chemical shifts are referred to the solvent or to phosphoric acid. Mass spectra were determined with VG Micromass ZAB 1F and 16F instruments. Microanalyses were performed by Dr. F. B. Strauss of this laboratory. All reagents commercially available (Aldrich, BDH, Johnson Matthey or Sigma) were of the best grade and used without further purification. Disodium tetrachloropalladate,[28] *E*-2,2-dimethylcyclohexanone oxime,[15] 2,2,6,6-tetramethylcyclohexanone oxime,[17] *E*-lupanone oxime,[25] and the organo-palladium derivatives (3), (4), and (5)[5] were prepared according to the literature procedures.

Palladation of Oximes. *Isolation of Compounds* (13), (17), (27), *and* (38). *General Procedure*.- A solution of disodium tetrachloropalladate (1.2 mmol), sodium acetate (1.2 mmol), and the corresponding oxime (1 mmol) in ethanol (10 ml) was stirred at room temperature for *ca*. 3 d. The solvent was removed under reduced pressure (15 mmHg), the residue was dissolved in dichloromethane (3 x 20 ml), and the solution filtered through celite. The solvent was evaporated to give the crude palladated oxime, which was purified by recrystallization.

Compound (13, m.p. 135-138°C (hexane-chloroform); ν(CCl_4) 3360 (OH), 1740 (C=O), and 1655 cm^{-1} (C=N); δ_H 1.18 (3 H, s, CH_3C), 1.87 (3 H, s, CH_3CN), 2.16 (3 H, s, CH_3CO), 2.34, 2.63 (2 H, 2 d, *J* 8.4 Hz, CH_2Pd), 3.96, 4.01 (2 H, 2 d, *J* 11.3 Hz, CH_2O), and 8.27 (1H, br s, OH); δ_C 12.75 (q, $\underline{C}H_3CN$), 20.93 (g, $\underline{C}H_3CO$), 22.23 (q, $\underline{C}H_3CC$), 33.67 (br t, CH_2Pd), 52.90 (s, $\underline{C}CH_2$), 68.84 (t, CH_2O), 170.58 (s, C=O), and 173.11 ppm (s, C=N).

Compound (17), m.p. 182-185°C (dec.) (methanol) (Found: C, 34.6; H, 5.1; N, 5.1; Cl, 12.6. $C_{16}H_{28}Cl_2N_2O_2Pd_2$ requires C, 34.07; H, 5.00; N, 4.96; Cl, 12.57); ν(Nujol) 3440 (OH), and 1650 cm^{-1} (C=N); δ_H 1.29 (3 H, s, CH_3), 1.42-1.92 [7 H, m, $(CH_2)_3CCN$ and $CH_{ax}CN$], 2.51, 2.57 (2 H, 2 d, *J* 8.2 Hz, CH_2Pd), 3.05 (1H, m, $CH_{eq}CN$), and 8.15 (1 H, br s, OH); δ_C 21.76, 24.01, 24.47 [3 t, $(\underline{C}H_2)_3CCN$], 26.48 (q, CH_3), 39.65 (t, $\underline{C}H_2CN$), 40.40 (br t, CH_2Pd), 49.47 (s, $\underline{C}CH_3$), and 176.71 ppm (s, C=N); *m/e* 562 (M^+ for ^{35}Cl and ^{106}Pd).

Compound (27), m.p. 177-170°C (dec.) (hexane) (Found: C, 38.9; H, 6.2; N, 4.6. $C_{20}H_{36}Cl_2N_2O_2Pd_2$ requires C, 38.73; H, 5.85; N, 4.52); ν($CHCl_3$) 3370 (OH) and 1630 cm^{-1} (C=N); δ_H 1.24 (3 H, s, CH_3CCPd), 1.29-1.69 (12 H, m with 2 s at 1.37 and 1.49, 2 x CH_3 and 3 x CH_2), 2.33, 2.46 (2 H, 2 d, *J* 7.1 Hz, CH_2Pd), and 8.42 (1 H, br s, OH); δ_C 17.74, 36.46, 40.10 [3 t, $(CH_2)_3$], 25.51, 28.09, 31.04 (3 q, 3 x CH_3), 39.10, 51.19 (2 s, 2 x $\underline{C}CH_3$), 41.22 (br t, CH_2Pd), and 179.61 ppm (s, C=N).

Compound (38), m.p. >210°C (hexane-chloroform) (Found: C, 61.1; H, 8.6; N, 2.4. $C_{60}H_{100}Cl_2N_2O_2Pd_2$ requires C, 61.85; H, 8.65; N, 2.40); $[\alpha]^{20}_{D}$ -31.9°(c 1.0, $CHCl_3$); ν(CCl_4) 3360 cm^{-1} (OH); δ_H 0.76 (3 H, s, 28-CH_3), 0.77, 0.84 (6 H, 2 d, *J* 6.8 Hz, 29- and 30-CH_3), 0.91, 0.93 (6 H, 2 s, 26- and 27-CH_3), 0.95-1.94 [30 H, m with 2 s at 1.05 (25-CH_3) and 1.26 (24-CH_3), 2 x CH_3, 9 x CH_2, and 6 x CH], 2.03 (1 H, m, $CH_{ax}CN$), 2.50 (1 H, br signal, CHPd), 2.61 (1H, d, *J* 7.5 Hz, CHPd), 2.98 (1H, m, $CH_{eq}CN$), and 8.14 (1 H, br s, OH); δ_C 43.15 (br t, 23-CH_2Pd) and 177.69 ppm (s, C=N).

Preparation of Pyridine Complexes (18), (28), *and* (39). *General Procedure*.- To a solution of the dimeric organopalladium compound (17), (27), or (38) (0.1 mmol) in tetrahydrofuran (5 ml) was added pyridine (0.02 ml, 0.2 mmol) and the mixture was stirred for 10 min. The solvent was evaporated (15 mmHg) and the residue recrystallized to afford the corresponding complexes (18), (28), and (39).

Complex (18), m.p. 138-140°C (hexane-chloroform); ν($CHCl_3$) 3230, 3140 (OH), 1640 (C=N), and 1600 cm^{-1} (Py); δ_H 1.27 (3 H, s, CH_3), 1.45-1.92 (7 H, m, 3 x CH_2 and $CH_{ax}CN$), 2.11, 2.47 (2 H, 2 d, *J* 8.6 Hz, CH_2Pd), 3.08 (1H, m, $CH_{eq}CN$), 7.34, 7.78, 8.68 (5 H, 3 m, Py), and 9.93 (1 H, s, OH); δ_C 21.96, 24.10, 24.51 [3 t, $(CH_2)_3$], 26.89 (q, CH_3), 40.58 (t, $\underline{C}H_2CN$), 44.35 (t, CH_2Pd), 48.76 (s, $\underline{C}CH_3$), 124.98, 137.66, 152.49 (3 d, Py), and 176.77 ppm (s, C=N).

Complex (28), m.p. 170°C (dec.) (hexane-chloroform); ν(CCl_4) 3330, 3120 (OH), 1635 (C=N), and 1610 cm^{-1} (Py); δ_H 1.25 (3 H, s, CH_3CCPd), 1.30-1.72 [12 H, m with s at 1.40 and d at 1.49, *J* 1.3 Hz, $(CH_2)_3$ and 2 x CH_3], 1.91 (1H, d, *J* 7.5 Hz, CHPd), 2.42 (1 H, dd, *J* 7.5 and 1.4 Hz, CHPd), 7.33, 7.78, 8.67 (5 H, 3m, Py), and 10.16 (1H, s, OH); δ_C 18.04, 37.60, 40.19 [3 t, $(CH_2)_3$], 25.40, 28.13, 31.46 (3q, 3 x CH_3), 38.99, 50.56 (2 s, 2 x $\underline{C}CH_3$), 45.32 (t, CH_2Pd), 124.97, 137.60, 152.64 (3 d, Py), and 179.43 ppm (s, C=N).

Complex (39), m.p. 190°C (dec.) (hexene-chloroform); $[\alpha]^{20}_{D}$ -30.47°(c 1.8, $CHCl_3$); $\nu(CCl_4)$ 3165 (OH), 3080, and 1600 cm^{-1} (Py); δ_H 0.76 (3 H, s, 28-CH_3), 0.77, 0.85 (6 H, 2 d, *J* 6.8 Hz, 29- and 30-CH_3), 0.93, 0.94 (6H, 2 s, 26- and 27-CH_3), 0.98-1.97 [30 H, m with 2 s at 1.07 (25-CH_3) and 1.26 (24-CH_3), 2 x CH_3, 9 x CH_2, and 6 x CH], 2.00-2.17 92 H, m with d at 2.11, *J* 8.5 Hz, CHPd and $CH_{ax}CN$), 2.47 (1 H, d, *J* 8.5 Hz, CHPd), 3.04 (1 H, m, $CH_{eq}CN$). 7.34, 7.78, 8.67 (5 H, 3 m, Py), an 8.92 (1H, s, OH); δ_C 46.32 (t, 23-CH_2Pd), and 177.69 ppm (s, C=N).

Preparation of Triphylphosphine Complexes (14), (19), (26), (29), *and* (40). *General Procedure*.- A mixture of the dimeric organopalladium compound (13), (17), (27), or (38) (0.1 mmol) and triphenylphosphine (0.053 g, 0.2 mmol) in methanol (20 ml) was refluxed for 30 min. The solvent was evaporated (15 mmHg) and the residue was recrystallized to afford the complexes (14), (19), (29), or (40). In the case of the complex (26) the corresponding dimer prepared as it was above described was transformed in situ into the complex (26).

Complex (14), m.p. 130-132°C (ethanol); $\nu(CHCl_3)$ 3210, 3150 (OH), 1730 (C=O), 1640 (C=N), 1600, and 1570 cm^{-1} (Ph); δ_H 1.06 (3 H, s, CH_3C), 1.56 (1 H, dd, *J* 10.2 and $\underline{J}_{HP}$ 3.4 Hz, CHPd), 1.69 (1 H, dd, *J* 10.2 and $\underline{J}_{HP}$ 4.2 Hz, CHPd), 1.95 (3 H, s, CH_3CN), 2.05 (3 H, s, CH_3CO), 3.76, 3.97 (2 H, 2 d, *J*11.0 Hz, CH_2O), 7.37-7.52, 7.62-7.76 (15 H, 2m, 3 x Ph), and 10.63 (1H, d, $\underline{J}_{HP}$ 2.6 Hz, OH); δ_C 12.60 (q, $\underline{C}H_3CN$), 20.89 (q, $\underline{C}H_3CO$) 23.40 (q, $\underline{C}H_3C$), 40.47 (t, CH_2Pd), 52.48 (s, $\underline{C}CH_3$), 70.23 (t, CH_2O), 128.37 (dd, $\underline{J}_{CP}$ 11.0Hz, $CH_{\underline{m}}$), 130.60 (d, CH_p), 130.86 (d, J_{CP} 49.4 Hz, $C_{\underline{i}}$), 134.39 (dd, $\underline{J}_{CP}$ 12.7 Hz, CH_o), 170.60, and 171.29 (2 s, C=O and C=N); δ_P 30.37 ppm.

Complex (19), m.p. 196°C (dec.) (ethanol) (Found: C, 57.4; H, 5.4; N, 2.6; Cl, 6.5; P, 5.6. $C_{26}H_{29}ClNOPPd$ requires C, 57.37; H, 5.37; N, 2.57; Cl, 6.51; P, 5.69; ν(Nujol) 3130 (OH) and 3090 cm^{-1} (Ph); δ_H 1.17 (3 H, s, CH_3), 1.20-1.62, 1.76-2.02 (8 H, 2 m with dd at 1.33, *J* 9.6 and $\underline{J}_{HP}$ 7.4 Hz, 3 X CH_2 ring, CHPd, and $CH_{ax}CN$, 2.06 (1 H, d, *J* 9.6 Hz, CHPd), 3.12-3.25 (1H, m, $CH_{eq}CN$), 7.40, 7.67 (15 h, 2 m, 3 x Ph), and 10.46 (1H, d, $\underline{J}_{HP}$ 2.4 Hz, OH); δ_C 22.07, 23.75, 24.44 (3 t, 3 x CH_2 ring), 27.71 (q, CH_3), 40.77 (t, $\underline{C}H_2CN$), 47.76 (t, CH_2Pd), 49.15 (s, $\underline{C}CH_3$), 128.26 (dd, $\underline{J}_{CP}$ 10.0 Hz, $CH_{\underline{m}}$), 130.41 (d, $CH_{\underline{p}}$), 131.11 (d, $\underline{J}_{CP}$ 10.0 Hz, $CH_{\underline{m}}$), 130.41 (d, $CH_{\underline{p}}$), 131.11 (d, $\underline{J}_{CP}$ 48.8 HZ, $C_{\underline{i}}$), 134.40 (dd, $\underline{J}_{CP}$ 11.4 Hz, $Ch_{\underline{o}}$), and 175.17 (s, C=N); δ_P 30.94 ppm; *m/e* 508 (M^+ -35, for ^{35}Cl and ^{106}Pd).

Complex (26), m.p. 156-158°C (dec) (acetone-hexane); ν 3200 (OH), 1725 (C=O), 1670 (C=N), 1600, and 1585 cm^{-1} (Ph); δ_H 1.21-1.75 (7H, m with dd at 1.40, *J* 10.2 and $\underline{J}_{HP}$ 7.0 Hz, 3 x CH_2 ring and CHPd), 1.82-2.11 (5 H, m with d at 1.87, *J* 10.2 Hz, and s at 2.05, CHPh, $CH_{ax}CN$, and CH_3CO, 3.22 (1 H, m, $CH_{eq}CN$), 3.81, 4.28 (2 h, 2 d, *J* 10.8 Hz, CH_2O), 7.35-7.53, 7.62-7.81 (15 H, 2 m, 3 x Ph), and 10.67 (1 H, d, $\underline{J}_{HP}$ 3.0 Hz, OH); δ_C 21.03 (q, $\underline{C}H_3C$), 21.98, 24.09, 24.47 (3 t, 3 x CH_2 ring), 36.62 (t, $\underline{C}H_2CN$), 42.30 (t, CH_2Pd), 52.87 (s, $\underline{C}CN$), 68.29 (t, CH_2O) 128.31 (dd, $\underline{J}_{CP}$ 10.7 Hz, $CH_{\underline{m}}$), 130.53 (d, $CH_{\underline{p}}$), 130.94 (d, $\underline{J}_{CP}$ 50.8 Hz, $C_{\underline{i}}$), 134.40 (dd, $\underline{J}_{CP}$ 12.0 Hz, $CH_{\underline{o}}$), 170.63, and 171.46 (2 s, C=O and C=N); δ_P 30.49 ppm.

Complex (29), m.p. 192-193°C (ethanol); ν(Nujol) 3120 (OH) and 3040 cm^{-1} (Ph); δ_H 1.17 (1 H, dd, $\underline{J}=\underline{J}_{HP}$ 8.8 Hz, CHPd), 1.25-1.63 (15 H, m with 3 s at 1.28, 1.33, and 1.43, 3 x CH_3 an 3 x CH_2 ring), 2.11 (1 H, d, *J* 8.8 Hz, CHPd), 7.35-7.50, 7.60-7.75 (15 H, 2 m, 3 x Ph), and 10.71 (1 H, d, $\underline{J}_{HP}$ 3.0 Hz, OH); δ_C 18.16, 38.24, 40.56 (3 t, 3 x CH_2 ring), 25.39, 28.30, 32.42 (3 q, 3 x CH_3), 38.68, 50.77 (2 s, 2 x $\underline{C}CH_3$), 49.39 (t, CH_2Pd), 128.29 (dd, $\underline{J}_{CP}$ 10.8 Hz, $CH_{\underline{m}}$), 130.38 (d, $CH_{\underline{p}}$), 131.34 (d, $\underline{J}_{CP}$ 48.3 Hz, $C_{\underline{i}}$), 134.40 (dd, $\underline{J}_{CP}$ 11.7 Hz, $CH_{\underline{o}}$), and 177.76 (s, C=N); δ_P 30.75 ppm.

Complex (40), m.p.>210°C (hexane-chloroform); $[\alpha]^{20}_{D}$ -4.05°(c 1.48, $CHCl_3$); $\nu(CCl_3)$ 3160 (OH), 3070, 3050 (Ph), and 1665 cm^{-1} (C=N); δ_H 0.74 (3 H, s, 28-CH_3), 0.76, 0.84 (6H, 2 d, *J* 6.8 Hz, 29- and 30-CH_3), 0.88-1.95 [37 H, m with 3 s at 0.88, 0.99 (26- and 27-CH_3), and 1.08 (25-CH_3), and d at 1.27, *J* 3.3 Hz (24-CH_3), 3 x CH_3, 9 x CH_2, 6 x CH, and CHPd], 2.00-2.20 (2 H, m with d at 2.04, *J* 8.5 Hz, CHPd and $CH_{ax}CN$), 3.12 (1 H, m, $CH_{eq}CN$), 7.30-7.56, 7.64-7.80 (15 H, 2 m, 3 x Ph), and 10.43 (1 H, d, $\underline{J}_{HP}$ 2.6 Hz, OH); δ_P 30.83 ppm.

Preparation of O-Acetyl Pyridine Complexes (6), (20), *and* (30). *General Procedure*.- A mixture of the dimeric organopalladium compound (3), (17), or (27) (0.33 mmol), triethylamine (0.14 ml, 1.0 mmol), acetic anhydride (0.094 ml, 1.0 mmol), and 4-dimethylaminopyridine (6.0 mg, 0.05 mmol) in dichloromethane (20 ml) was stirred for 15 h at room temperature. The resulting solution was washed with diluted hydrochloric acid, sodium hydrogen carbonate, and water, the organic layer was dried ($MgSO_4$), and stirred with pyridine (0.052 ml, 0.66 mmol) for 10 min. The solvent was evaporated (15 mmHg) and the residue recrystallized to afford the corresponding complexes (6), (20), and (30).

Complex (6), m.p. 190°C (dec.) (hexane-chloroform); $\nu(CCl_4)$ 3070, 1600 (Py), 1775 (C=O), and 1645 cm^{-1} (C=N); δ_H 1.30 (6 H, s, 2 x CH_3C), 1.88 (3 H, s, CH_3CN), 2.31 (5 H, s, CH_3CO and CH_2Pd), 7.29, 7.75, and 8.75 (5 H, 3 m, Py); δ_C 14.04 (q, CH_3CN), 19.01 (q, CH_3CO), 27.98 (q, $\underline{C}H_3C$), 41.01 (t, CH_2Pd), 49.84 (s, $\underline{C}CH_3$), 124.76, 137.40, 152.75 (3 d, Py), 167.17 (s, C=N), an 192.04 ppm (s, C=O).

Complex (20), m.p. 139-140°C (hexane-chloroform); $\nu(CHCl_3)$ 3080, 1615, 1600 (Py), 1770 (C=O), and 1635 cm^{-1} (C=N); δ_H 1.44 (3 H, s, CH_3C), 1.51-2.10 (8 H, m with d at 2.03, *J* 7.4 Hz, 3 x CH_2 ring, CHPd, and $CH_{ax}CN$), 2.31 (3 H, s, CH_3CO), 2.46 (1 H, m, CHPd), 2.78 (1 H, m, $CH_{eq}CN$), 7.30, 7.74, and 8.72 (5 H, 3 m, Py); δ_C 18.95 (q, $\underline{C}H_3CO$), 21.61, 24.76, 26.18 (3 t, 3 x CH_2 ring), 27.38 (q, $\underline{C}H_3C$), 40.48, 42.42 (2 t, $\underline{C}H_2CN$ and CH_2Pd), 49.89 (s, $\underline{C}CH_3$), 124.73, 137.37, 152.72 (3 d, Py), 167.34 (s, C=N), and 193.74 ppm (s, C=O).

Complex (30), m.p. 125-127°C (hexane-chloroform); $\nu(CCl_4)$ 3100, 3080, 3050, 1615, 1600 (Py), 1780 (C=O), and 1640 cm^{-1} (C=N); δ_H 1.17-1.77 (15 H, m with 3 s at 1.25, 1.31, an 1.66, 3 x CH_3C and 3 x CH_2 ring), 1.84 (1 H, d, *J* 7.5 Hz, CHPd), 2.32 (3 H, s, CH_3CO), 2.46 (1 H, m, CHPd), 7.31, 7.75, and 8.70 (5 H, 3 m, Py); δ_C 17.76, 37.85, 40.80 (3 t, 3 x CH_2 ring), 19.89 (q, $\underline{C}H_3CO$, 26.64, 28.60, 31.64 (3 q, 3 x $\underline{C}H_3C$), 40.14, 51.72 (2 s, 2 x $\underline{C}CH_3$), 43.79 (t, CH_2PH), 124.70, 137.22, 152.94 (3 d, Py), 167.79 (s, C=N), and 194.02 ppm (br s, C=O).

Preparation of the Deuteriated Oximes (7), (15) (21), (31), *and* (41). *General Procedure*.- To a solution of the dimeric organopalladium compound (3), (13), (17), (27), or (38) (0.5 mmol) in tetrahydrofuran (8 ml) and methanol (2 ml) was added a solution of sodium cyanoborodeuteride (0.066g, 1 mmol) in tetrahydrofuran (4 ml) and methanol (1 ml) at 0°C and the mixture was stirred for 1 h allowing to warm it till room temperature. The black precipitate was filtered off, the solvents were evaporated (15 mmHg) and the residue hyrolysed with water, extracted with dichloromethane, the organic layer dried ($MgSO_4$), and evaporated (15 mmHg). The resulting residue was recrystallized to afford the deuteriated oximes (7), (15), (21), (31), and (41).

E-4-*Deuteriopinacolone Oxime* (7), m.p. 77-78°C (hexane-chloroform); ν(Nujol) 3240 (OH) and 1650 cm^{-1} (C=N); δ_H 1.12 (2H, s, CH_2D), 1.14 (6 H, s, 2 x CH_3C), 1.88 (3H, s, CH_3CN), and 9.17 (1H, br s, OH); δ_D ($CHCl_3$) 1.165 (CH_2D); δ_C 9.86 (q, $\underline{C}H_3CN$), 27.22 (tt, J_{CD} 18.9 Hz, CH_2D), 27.51 (q, $\underline{C}H_3C$), 37.08 (s, $\underline{C}CH_3$), and 164.63 ppm (s, C=N); *m/e* 116 (M^+).

E-1-*Acetoxy*-2-*deuteriomethyl*-2-*methylbutan*-3-*one Oxime*. (15), m.p. 85-86°C (hexane); ν(Nujol) 3250 (OH), 1730 (C=O), and 1645 cm^{-1} (C=N); δ_H 1.16 (5 H, s, CH_3C and CH_2D), 1.87 (3 H, s, CH_3CN), 2.07 (3 H, s, CH_3CO), 4.06 (2 H, s, CH_2O), and *ca*. 8.10 (1 H, br s, OH); δ_D ($CHCl_3$) 1.185 (CH_2D); δ_C 9.95 (q, $\underline{C}H_3CN$), 20.86 (q, $\underline{C}H_3CO$), 22.47 (tt, J_{CD} 19.7 Hz, CH_2D), 27.77 (q, $\underline{C}H_3C$), 40.56 (s, $\underline{C}CH_3$), 70.04 (t, CH_2O), 161.24 (s, C=N), and 170.98 ppm (s, C=O); *m/e* (DCI, NH_3) (M^++2).

E-2-*Deuteriomethyl*-2-*methycyclohexanone Oxime* (21), m.p. 91-92°C (hexane) (Found: C, 67.5; H/D, 10.7; N, 9.5. $C_8H_{14}DNO$ requires C, 67.56; H/D, 11.34; N, 9.85); $\nu(CHCl_3)$ 3260 (OH) and 1660 cm^{-1} (C=N); δ_H 1.05 (2 H, s, CH_2D), 1.13 (3 H, s, CH_3), 1.44, 1.54 (6 H, 2 m, 3 x CH_2 ring), 2.56 (2H, m, CH_2CN), and 8.77 (1H, br s, OH); δ_D ($CHCl_3$) 1.185 (CH_2D); δ_D 20.72, 21.74, 26.07 (3 t, 3 x CH_2 ring), 26.30 (tt, J_{CD} 18.7 Hz, CH_2D), 26.58 (q, CH_3), 37.51 (s, $\underline{C}CH_3$), 41.24 (t, $\underline{C}H_2CN$), and 165.63 ppm (s, C=N); *m/e* 142 (M^+).

E-2-Deuteriomethyl-2,6,6-trimethylcyclohexanone Oxime (31), m.p. 152-154°C (hexane-chloroform); ν(Nujol) 3300, 3220 (OH), and 1650 cm^{-1} (C=N); δ_H 1.17, 1.18, 1.35 (11 H, 3 s, CH$_2$D and 3 x CH$_3$), 1.49-1.69 (6H, 2 m, 3 x CH$_2$ ring), and 7.97 (1 H, br s, OH); δ_D 9CHCl$_3$) 1.223 9CH$_2$D); δ_C 17.46, 37.65. 40.61 (3 t, 3 x CH$_2$ ring), 26.90, 30.59 (2 q, 3 x CH$_3$), 30.31 (tt, J_{CD} 20.1 Hz, CH$_2$D), 37.04, 41.68 (2s, 2 x CCH$_3$), and 168.25 ppm (s, C=N); m/e 170 (M$^+$).

E-23-Deuteriolupanone Oxime (41), m.p.>210°C (ethyl acetate-chloroform); ν(Nujol) 3240 (OH) and 1650 cm^{-1} (C=N); δ_H 0.76 (3 H, s, 28-CH$_3$), 0.76, 0.84 (6H, 2 d, J 6.7, 29- and 30-CH$_3$), 0.92, 0.95 (6 H, 2 s, 26- and 27-CH$_3$), 0.97-2.00 [32 H, m with 2 s at 1.05 and 1.07 (24- and 25-CH$_3$), and d at 1.13, J 5.6 Hz (23-CH$_2$D), 2 x CH$_3$, 9 x CH$_2$ and 6 x CH], 2.26, 2.98 (2H, 2 m, CH$_2$CN), and 7.27 (1 H, br s, OH); δ_D (CH$_2$Cl$_2$) 1.14 (CH$_2$D); δ_C 27.07 (tt, J_{CD} = 19 Hz, CH$_2$D), and 167.49 ppm (s, C=N);[29] m/e (DCI, NH$_3$) 444 (M$^+$+2).

Chlorination of Compound (3). E-4-Chloropinacolone Oxime (8).- Through a solution of compound (3) (0.147 g, 0.287 mmol) in carbon tetrachloride (20 ml) was bubbled chlorine for 30 min. The solvent was evaporated and the residue dissolved in tetrahydrofuran (4 ml) and methanol (1 ml). To the resulting solution was added sodium cyanoborohydride (0.038 g, 0.574 mmol) in tetrahydrofuran (4 ml) and methanol (1 ml) at 0°C and the mixture was stirred for 30 min. The black precipitate was filtered off, the solvents were evaporated (15 mmHg), and the residue was extracted with ether. The solvent was removed (15 mmHg) to afford the title compound (0.055 g, 64%), m.p. 60-62°C (hexane); ν(CHCl$_3$) 3300 (OH) and 1660 cm^{-1} (C=N); δ_H 1.23 (6H, s, 2 x CH$_3$C), 1.90 (3 H, s, CH$_3$CN), 3.57 (2 H, s, CH$_2$Cl), and 8.79 (1 H, br s, OH); δ_C 10.01 (q, CH$_3$CN), 23.64 (q, 2 x CH$_3$C), 42.25 (s, CCH$_3$), 52.73 (t, CH$_2$Cl), and 160.99 ppm (s, C=N); m/e 150 (M$^+$+1, for ^{35}Cl).

Oxidation of Organopalladium Compounds (3), (13), (17), (20), (27), (30), and (38) with Lead Tetraacetate (Pd:Pb molar ratio 1:1). Isolation of Acetoxy Derivatives (9), (11), (16), (22), (23), (32), and (42). General Procedure.- To a solution of the dimeric organopalladium compound (3), (13), or (17) (0.4 mmol) in tetrahydrofuran (15 ml) was added pyridine (0.06 ml, 0.8 mmol) and stirred for 10 min. Then, a solution of lead tetraacetate (0.35 g, 0.8 mmol) in acetic acid (5 ml) was added to the resulting pyridine complex at 0°C, and the mixture was stirred for 2 h allowing to rise the temperature to 20°C. A solution of sodium borohydride (0.03 g, 0.8 mmol) in 1 N aqueous sodium hydroxide (5 ml) was then added, and stirred for 30 min. The black suspension was filtered, the filtrate was extracted with ether, washed with water and sodium hydrogen carbonate, dried (MgSO$_4$), and evaporated (15 mmHg) to afford the products (9), (16), and (22), which were distilled and/or recrystallized. In the case of the preparation of products (23) and (32) the oxidation was carried out as it was above described starting directly from the pyridine complexes (20) and (30). In the case of the oxidation of compounds (3) and (38) to give the products (11) and (42), respectively, the acetylation of the corresponding dimeric organopalladium compound was carried out prior to the in situ oxidation, which was performed as it was above described.

E-4-Acetoxypinacolone Oxime (9), m.p. 85-86°C (hexane) (Found: C, 55.9; H, 8.8; N, 7.9 C$_8$H$_{15}$NO$_3$ requires C, 55.47; H, 8.73; N, 8.09; ν(Nujol) 3250 (OH), 1730 (C=O), and 1645 cm^{-1} (C=N); δ_H 1.15 (6 H, s, 2 x CH$_3$C), 1.87 (3 H, s, CH$_3$CN), 2.06 (3 H, s, CH$_3$CO), 4.07 (2 H, s, CH$_2$O), and 8.46 (1 H, s, OH); δ_C 10.03 (q, CH$_3$CN), 20.83 (q, CH$_3$CO), 22.77 (q, CH$_3$C), 40.60 (s, CCH$_3$), 70.01 (t, CH$_2$O), 161.10(s, C=N), and 170.98 ppm (s, C=O); m/e (CI, NH$_3$) 175 (M$^+$+2).

E-4-Acetoxy-O-acetylpinacolone Oxime (11), oil; ν(neat) 1740 (C=O) and 1630 cm^{-1} (C=N); δ_H 1.22 (6 H, s, 2 x CH$_3$CN), 2.05 (3 H, s, CH$_3$CO$_2$C), 2.19 (3 H, s, CH$_3$CO$_2$N), and 4.10 (2H, s, CH$_2$O); δ_C 12.05 (q, CH$_3$CN), 19.87, 20.79 (2 q, 2 x CH$_3$CO), 22.68 (q, CH$_3$C), 41.52 (s, CCH$_3$), 69.68 (t, CH$_2$O), 168.35, 169.29, and 170.76 ppm (3 s, C=N and 2 x C=O); m/e (DCI, NH$_3$) 216 (M$^+$+1).

E-1-Acetoxy-2-acetoxymethyl-2-methylbutan-3-one Oxime (16), m.p. 45-47°C (hexane-chloroform); ν(CCl$_4$) 3460, 3315 (OH), 1735 (C=O), and 1640 cm^{-1} (C=N); δ_H (3 H, s, CH$_3$C), 1.88 (3 H, s, CH$_3$CN), 2.06 (6H, s, 2 x CH$_3$CO), 4.16, 4.21 (4H, 2 d, J 11.5 Hz, 2 x CH$_2$O), and 8.13 (1 H, br s, OH); δ_C 10.03 (q, CH$_3$CN), 18.22 (q, CH$_3$C), 20.79 (q, CH$_3$CO), 43.91 (s, CCH$_3$), 65.70 (t, CH$_2$O), 158.35 (s, C=N), and 170.76 ppm (s, C=O); m/e (CI, NH$_3$) 233 (M$^+$+2).

E-2-Acetoxymethyl-2-methylcyclohexanone Oxime (22), b.p. 125°C (0.1 mmHg, Kugelrohr); ν(neat) 3400 (OH), 1740 (C=O), and 1650 cm^{-1} (C=N); δ_H 1.17 (3 H, s, CH_3C), 1.46-1.73 (6H, m, 3 x CH_2 ring), 2.06 (3 H, s, CH_3CO), 2.51-2.66 (2H, m, CH_2CN), 4.08, 4.20 (2 H, 2d, J 11.0 Hz, CH_2O), and 8.96 (1H, br s, OH); δ_C 20.84, 21.21, 25.51 (3 t, 3 x CH_2 ring), 20.84 (q, $\underline{C}H_3CO$), 21.94 (q, $\underline{C}H_3C$), 36.13 (t, $\underline{C}H_2CN$), 40.89 (s, $\underline{C}CH_3$), 69.10 (t, CH_2O), 162.16 (s, C=N), and 171.07 ppm (s, C=O); m/e 199 (M$^+$).

E-2-Acetoxymethyl-O-acetyl-2-methylcyclohexanone Oxime (23), oil; ν(CCl_4) 1750 (C=O), and 1625 cm^{-1} (C=N); δ_H 1.26 (3 H, s, CH_3C), 1.55-1.78 (6 H, m, 3 x CH_2 ring), 2.07, 2.18 (6 H, 2 s, 2 x CH_3CO), 2.60 (2H, m, CH_2CN), 4.2, and 4.34 (2 H, 2 d, J 11.2 Hz, CH_2O); δ_C 19.90, 20.38 (2 q, 2 x $\underline{C}H_3CO$), 20.49, 23.26, 25.65 (3 t, 3 x CH_2 ring), 22.01 (q, $\underline{C}H_3C$), 36.29 (t, $\underline{C}H_2CN$), 41.91 (s, $\underline{C}CH_3$), 68.82 (t, CH_2O), 169.53, 169.78 and 170.88 ppm (3 s, C=N and 2 x C=O); m/e (CI, NH_3) 242 (M$^+$+1).

E-2-Acetoxymethyl-O-acetyl-2,6,6-triemthylcyclohexanone oxime (32), oil; ν(neat) 1745 (C=O) and 1630 cm^{-1} (C=N); δ_H 1.29, 1.33 (9 H, 2 s, 3 xCH_3), 1.47-1.80 (6 H, m, 3 x CH_2 ring), 2.06, 2.19 (6 H, 2 s, 2 x CH_3CO), 4.07, and 4.31 (2 H, 2 d, J 10.7 Hz, CH_2O); δ_C 17.04, 32.80, 40.51 (3 t, 3 x CH_2 ring), 20.07, 20.87 (2 q, 2 x $\underline{C}H_3CO$), 26.51, 27.53, 27.69 (3 q, 3 x $\underline{C}H_3C$), 37.86, 42.22 (2 s, 2 x $\underline{C}CH_3$), 71.34 (t, CH_2O), 169.16, 170.78 and 172.85 ppm (3 s, C=N and 2 x C=O); m/e (CI, NH_3) 270 (M$^+$+1).

23-Acetoxy-O-acetyllupanone Oxime (42), oil; $[\alpha]^{20}_D$ +16.55°(c 1.4, $CHCl_3$); ν(neat) 1740 (C=O) and 1626 cm^{-1} (C=N); δ_H 0.76 (3 H, s, 28-CH_3), 0.76, 0.84 (6 H, 2 d, J 6.7 Hz, 29- and 30-CH_3), 0.90, 0.93 (6 H, 2 s, 26- and 27-CH_3), 0.97-1.91 [30 H, m with 2 s at 1.07 (25-CH_3), and 1.17 (24-CH_3), 2 x CH_3, 9 x CH_2, and 6 x CH], 2.06, 2.17 (6 H, 2 s, 2 x CH_3CO), 2.64 (2 H, m, CH_2CN), 4.09, and 4.19 (2H, 2 d, J 11.0 Hz, CH_2O); δ_C 68.29 (t, CH_2O), 169.65, and 170.84 ppm (2 s, C=N and 2 x C=O); m/e (DCI, NH_3) 543 (M$^+$+2).

Oxidation of Organopalladium Compounds (3) and (17) with Lead Tetraacetate (Pd:Pb molar ratio 1:2). Isolation of Compounds (12) and (24). General Procedure.- A mixture of dimeric organopalladium compound (3) or (17) (0.4 mmol) and pyridine (0.063 ml, 0.8 mmol) in tetrahydrofuran (10 ml) was stirred for 10 min. The solvent was evaporated (15 mmHg), the residue was suspended in acetic acid (5 ml) and a solution of lead tetraacetate (0.35 g, 0.8 mmol) in acetic acid (5 ml) was added to the resulting suspension. The mixture was refluxed for 2 h, cooled at room temperature, the solvent was evaporated (15 mmHg) and the residue was washed with an aqueous solution of sodium hydrogen carbonate, extracted with ether, and the ethereal layer washed with water and dried ($MgSO_4$). The evaporation of the solvent (15 mmHg) afforded the crude product (12) or (24), which was purified by distillation under reduced pressure.

4-Acetoxypinacolone (12), b.p. 100°C (0.1 mmHg, Kugelrohr); ν(neat) 1750 and 1710 cm^{-1} (C=O); δ_H 1.16 (6H, s, 2 x CH_3C), 2.03 (3 H, s, CH_3CO_2), 2.16 (3 H, s, CH_3CO) and 4.10 (2 H, s, CH_2O); δ_C 20.68 (q, $\underline{C}H_3CO_2$), 21.68 (q, $\underline{C}H_3C$), 25.33 (q, $\underline{C}H_3CO$), 47.56(s, $\underline{C}CH_3$), 69.82 (t, CH_2O), 170.66 (s, OC=O), and 210.89 ppm (s, C=O); m/e (CI, NH_3) 160 (M$^+$+2).

2-Acetoxymethyl-2-methylcyclohexanone (24), b.p. 130°C (0.1 mmHg, Kugelrohr); ν(neat) 1745 and 1715 cm^{-1} (C=O); δ_H 1.14 (3 H, s, CH_3C), 1.63-1.96 (6 H, m, 3 x CH_2 ring), 2.04 (3 H, s, CH_3CO_2), 2.36-2.53 (2 H, m, CH_2CO), 4.12, and 4.17 (2 H, 2 d, J 11.0 Hz, CH_2O); δ_C 20.65, 20.81 (2 q, $\underline{C}H_3C$ and $\underline{C}H_3CO$), 20.95, 27.08, 36.16, 38.77 (4 t, 4 x CH_2 ring), 48.59 (s, $\underline{C}CH_3$), 68.67 (t, CH_2O), 170.92 (s, OC=O), and 212.88 ppm (s, C=O); m/e (DCI, NH_3) 186 (M$^+$+2).

Hydrolysis of 4-Acetoxypinacolone Oxime (9). 4-Hydroxypinacolone Oxime (10). A mixture of compound (9) (0.155 g, 0.89 mmol) and potassium hydroxide (0.050 g, 1.0 mmol) in ethanol (15 ml) was refluxed for 15 h. After cooling the solvent was evaporated (15 mmHg) an the residue was treated with water (2 ml) and extracted with dichloromethane. The organic layer was dried ($MgSO_4$) and the solvent evaporated (15 mmHg). The residue was recrystallized (hexane-chloroform) to afford the title compound (0.041 g, 35%), m.p. 80-82°C (Lit.[20] m.p. 82°C); ν(Nujol) 3300 (OH) and 1640 cm^{-1} (C=N); δ_H ($CDCl_3$-D_2O) 1.06 (6 H, s, 2 x CH_3C), and 3.54 (2 H, s, CH_2O); δ_C 10.02 (q, $\underline{C}H_3CN$), 22.70 (q, $\underline{C}H_3C$), 42.13 (s, $\underline{C}CH_3$) 70.15 (t, CH_2O), and 163.54 ppm (s, C=N); m/e (CI, NH_3) 133 (M$^+$+2).

X-Ray Structure determination for the pyridine complex (18). Crystal Data $C_{13}H_{19}N_2OPdCl$ M = 361.16, monoclinic, a = 10.648(4) b = 14.769(3), c = 9.620(2) Å, β = 106.83(2)°, U = 1448.1 $Å^3$, Z = 4, D_c = 1.656 g cm^{-3}, $\mu(Mo - K_\alpha)$ = 14.3 cm^{-1}. Space group $P2_1/c$.

An orange crystal of the pyridine complex (18) was obtained by recrystallisation from dichloromethane/hexane which had approximate dimensions of 0.48 x 0.63 x 0.73 mm. Data collection was performed with a CAD-4 computer controlled diffractometer, equipped with a graphite monochromator. Data were collected using the ω-2θ scan technique for reflections in the range $0 < 2\theta < 55°$. The scan rate varied between 1.1 and 6.7 deg/min depending upon the intensity of the reflection. A total of 3325 unique reflections were measured which were corrected for Lorentz polarisation and absorption effects (relative transmission factors 1.78 - 2.01)[31] and gave 2874 reflections with $I > 3(\sigma)I$ which were used in subsequent calculations. The structure was solved by Patterson and electron density methods, and refined by full matrix least squares, first with isotropic and followed by anisotropic temperature factors. All hydrogen atoms were located in difference Fourier maps and were made to 'ride' on the atoms to which they were bonded. One reflection which showed gross extinction effects was omited from the refinement. The weight for each reflection was calculated from a three term Chebyshev series whose coefficients were 3122.6, 4342.1 and 1313.9.[32]

The refinement converged with a final R value of 0.042 (R_w = 0.043). All calculations were performed with the CRYSTALS[33] package on the Chemical Crystallography Laboratory VAX 11/750 computer.

Tables of atomic coordinates, bond lengths and bond angles have been deposited at the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW.

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