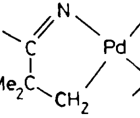
Palladation of Dimethylhydrazones, Oximes, and Oxime *O*-Allyl Ethers: Crystal Structure of $[Pd_3(ON{=}CPr^iPh)_6]$†

By Anthony G. Constable, Walter S. McDonald,* Lynne C. Sawkins, and Bernard L. Shaw*

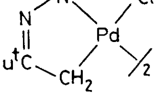
(*School of Chemistry, The University, Leeds* LS2 9JT)

Summary The oxime of isopropyl phenyl ketone (*Z*-isomer) with $NaOAc–Na_2PdCl_4$ gives $[Pd_3(ON{=}CPr^iPh)_6]$ and whereas pinacolone oxime carbopalladates regiospecifically on the t-butyl group, the dimethylhydrazone carbopalladates only on the methyl group: acetone oxime *O*-allyl ether palladates on the central carbon atom of the allyl group with nucleophilic attack (*e.g.* by OMe^-) on the terminal carbon atom.

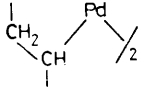
Organopalladium compounds are increasingly used in synthesis (see refs. 1—3 for recent examples). We have been investigating the palladation of simple derivatives of ketones which might be useful in synthesis and have studied oximes and *NN*-dimethylhydrazones since oximato (=NOH) and dimethylhydrazido ($=NNMe_2$) are quite commonly used as protecting groups for ketones.[4-8] We are particularly interested in the palladation of saturated aliphatic groups which, apart from 8-alkylquinolines,[9,10] is uncommon (or unknown) for nitrogen donors, whereas the palladation of aromatic rings, '*ortho*-palladation' is now well established. It has been reported that the *Z*-form (**1**) of the oxime of isopropyl phenyl ketone, when treated with Li_2PdCl_4 and sodium acetate gives an unidentified product whereas the *E*-form (**2**) undergoes *ortho*-palladation.[1]



(1)



(2)



(3)

(4)

(5)

(6)

---

† No reprints available.

It seemed possible that this unidentified product contained a palladated isopropyl group but we have found it to be a trinuclear complex $[Pd_3(ON{=}CPr^iPh)_6]$.‡ The detailed structure of this unusual complex has been determined by single crystal *X*-ray diffraction. Crystals are triclinic, space group $P\bar{1}$, with $a = 14{\cdot}843(4)$, $b = 19{\cdot}542(6)$, $c = 13{\cdot}396(4)$ Å, $\alpha = 97{\cdot}99(3)$, $\beta = 115{\cdot}91(3)$, $\gamma = 87{\cdot}26(3)°$, and $Z = 2$. The molecular structure, based on 3423 independent F_0 and refined to $R = 7{\cdot}3\%$ with anisotropic temperature factors for Pd only, is shown in the Figure. The molecule has approximate C_{3h} symmetry.§

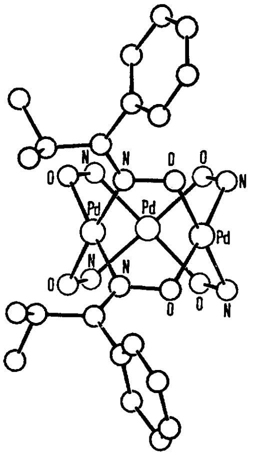


FIGURE. The molecular structure of $[Pd_3(ON{=}CPr^iPh)_6]$. For clarity the $=CPr^iPh$ unit is shown for only two of the six ligands. Principal bond lengths are Pd–O, 2·00—2·03(2); Pd–N, 1·99—2·03(2); and N–O, 1·34—1·37(3), while the Pd · · · Pd distances are 2·887, 2·908, and 2·901(3) Å.

Since steric effects can promote cyclopalladation reactions (with tertiary phosphines) we have also studied t-butyl phenyl ketone oxime, which exists only in the *Z*-form (**3**) (R = Ph, Y = OH). This carbopalladates smoothly on the t-butyl group to give (**4**) (R = Ph), when treated with Na_2PdCl_4–NaOAc. Similarly t-butyl methyl ketone oxime (pinacolone oxime) (**3**) (R = Me, Y = OH) and the corresponding ethyl derivative (**3**) (R = Et) palladate in high yield on the t-butyl group to give (**4**) (R = Me or Et). The structure of complex (**4**) (R = Me), has been determined by *X*-ray diffraction. In contrast, the dimethylhydrazone of pinacolone palladates regiospecifically on the (–N=CMe) methyl group when treated with Na_2PdCl_4–NaOAc to give (**5**): this was converted into the mononuclear acetylacetonate whose structure has also been determined by *X*-ray diffraction. Thus one gets different but complete regiospecificity in palladation depending on whether the oxime or dimethylhydrazone is used. In contrast, we find that the dimethylhydrazones of mixed aliphatic–aromatic ketones preferentially undergo *ortho*-palladation and in such cases the first nitrogen (=N–) is ligating in preference to the NMe_2 nitrogen [which is ligating in (**5**)]. This has been shown by *X*-ray diffraction for the cyclopalladated dimethylhydrazone of 4-methoxyacetophenone *i.e.* $[Pd_2Cl_2\{Me_2NN{=}C(Me)C_6H_4OMe\text{-}4\}_2]$. Oximes or dimethylhydrazones (L) of other purely aliphatic ketones which do not have a group as bulky as t-butyl, *e.g.*, isopropyl methyl ketone, diethyl ketone, or cyclohexanone, readily give complexes of type $[PdCl_2L_2]$ but attempts at carbopalladation using sodium acetate give very unstable products, which we have so far failed to isolate.

Allyldimethylamine, when treated with lithium chloropalladate in methanol, carbopalladates with nucleophilic attack (by OMe^-) on the central carbon atom of the allyl group to give a palladocycle $[Pd_2Cl_2\{Me_2NCH_2CH(OMe)CH_2\}_2]$.[12] Analogous reactions have been shown to occur with a variety of nucleophiles and allylic groups and the nucleophilic attack has been shown to be stereospecifically *trans*.[12–14] Two carbopalladations of this type have been used in a stereospecific synthesis of prostaglandin $PGF_{2\alpha}$.[15] We now find that oxime *O*-allyl ethers, *e.g.* $Me_2C{=}NOCH_2\text{-}CH{=}CH_2$ (readily prepared from acetoxime + allyl bromide + base), when treated with Na_2PdCl_4 in methanol in the presence of sodium acetate, undergo carbopalladation with nucleophilic attack (by OMe^-) on the terminal allylic carbon atom to give (**6**). This reaction could probably be extended to other allylic groups, nucleophiles, and oximes and be synthetically useful since it complements the carbopalladation of allylic amines described above where nucleophilic attack occurs on the central carbon atom of the allylic group.

We thank the S.R.C. for support.

(*Received, 23rd August* 1978; *Com.* 925.)

---

‡ This, and other complexes reported here have been fully characterized by elemental analysis, molecular weight determination, and ^1H n.m.r., i.r., and sometimes mass spectrometry.

§ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

[1] J. B. Melpolder and R. F. Heck, *J. Org. Chem.*, 1976, **41**, 265 and references therein.
[2] B. M. Trost, L. Weber, P. Strege, T. J. Fullerton, and T. J. Dietsche, *J. Amer. Chem. Soc.*, 1978, **100**, 3426 and references therein.
[3] R. A. Holton and R. G. Davis, *J. Amer. Chem. Soc.*, 1977, **99**, 4175.
[4] H. J. E. Loewanthal, in 'Protective Groups in Organic Chemistry,' ed. J. F. W. McOmie, Plenum Press, London and New York, 1973, pp. 341—342.
[5] E. J. Corey and D. Enders, *Tetrahedron Letters*, 1976, 11.
[6] W. G. Kofron and Ming-Kuo Yeh, *J. Org. Chem.*, 1976, **41**, 439.
[7] M. Avaro, J. Levisalles, and H. Rudler, *Chem. Comm.*, 1969, 445.
[8] V. Jäger and H. Grund, *Angew. Chem. Internat. Edn.*, 1976, **15**, 50.
[9] J. E. Hartwell, R. V. Lawrence, and M. J. Smas, *Chem. Comm.*, 1970, 912.
[10] V. I. Sokolov, T. A. Sorokina, L. L. Troitskaya, L. I. Solovieva, and O. A. Reutov, *J. Organometallic Chem.*, 1972, **36**, 389.
[11] H. Onoue, K. Minami, and K. Nakagawa, *Bull. Chem. Soc. Japan*, 1970, **43**, 3480.
[12] A. C. Cope, J. M. Kliegman, and E. C. Friedrich, *J. Amer. Chem. Soc.*, 1967, **89**, 287.
[13] P. M. Maitlis, 'The Organic Chemistry of Palladium,' Vol. II, Academic Press, New York, 1971, pp. 5—18.
[14] R. A. Holton and R. A. Kjonaas, *J. Amer. Chem. Soc.*, 1977, **99**, 4177.
[15] R. A. Holton, *J. Amer. Chem. Soc.*, 1977, **99**, 8083.