Preparation and Ring Inversion of some Highly Puckered Palladacyclobutan-3-one Complexes

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A high yield synthesis of a variety of highly puckered palladacyclobutan-3-one complexes which exhibit inversion in solution is described.

Interest in the chemistry of metallacyclobutanes has arisen since such systems have been implicated in several metal-catalysed reactions.[1–4] At the present time, however, there is little information on related metallacyclobutan-3-one complexes. We have previously described some platinacyclobutan-3-one complexes,[5] which contain a highly puckered ring, and an iridacyclobutan-3-one complex of unknown geometry has recently been reported.[6] We now describe a high yield synthesis of a variety of palladacyclobutan-3-one complexes **(1)** which contain a highly puckered metallacyclic ring exhibiting inversion in solution.

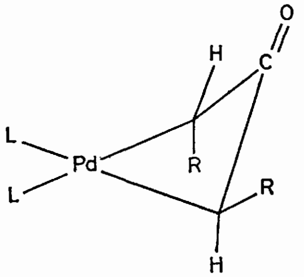
Reaction of $[Pd_2(dba)_3]$[7] (dba = dibenzylideneacetone) with dimethyl 3-oxoglutarate in the presence of dioxygen and triphenylphosphine in dry diethyl ether gives (80%) the white crystalline air-stable palladacyclobutan-3-one complex **(1a)**. High yields of the palladacyclobutan-3-one complexes **(1b)**—**(1e)** can similarly be obtained. These reactions appear to proceed *via* intermediate palladium dioxygen complexes since **(1a)** can also be obtained by the reaction of dimethyl 3-oxoglutarate with $[PdO_2(PPh_3)_2]$. Subsequent formation of the palladium–carbon σ-bonds may proceed *via* transfer of hydrogen from dimethyl 3-oxoglutarate to co-ordinated dioxygen as has been proposed in the formation of acetonylcobalt(III) complexes which are formed upon treatment of cobalt(II) complexes with acetone in the presence of dioxygen.[8–10]

In common with the platinum analogue of **(1a)** which has a highly non-planar ring,[5] the complexes **(1)** also have puckered palladacyclobutan-3-one rings in the solid state. The *X*-ray crystal structures of complexes **(1a)**, **(1d)**, and **(1e)** have been determined, and will be published separately; the geometries of their ring systems are very similar (Table 1). The extent of non-planarity and shortness of the Pd . . . C(2) distances suggest that a bonding description of **(1)** should include a contribution from the allylic structure **(2)**. A similar description to **(2)** has been proposed for trimethylenemethane–palladium complexes **(3)**; calculations show that a dihedral angle of 96° between the P–Pd–P and trimethylenemethane planes gives the minimum energy conformation, although the Pd–C distances were fixed in the calculation.[11]

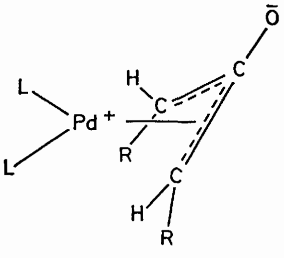
The puckering of the metallacyclobutanone ring is not a feature of saturated metallacyclobutanes. The crystal structure of $[PtCH_2CH_2CH_2(bipy)]$ (bipy = 2,2′-bipyridyl) shows the molecule to be almost completely planar with unexceptional C–C bond lengths of 1.53(1) Å. However the ^1H n.m.r. spectrum shows unusually large platinum coupling to the β-protons, and the possibility of a facile puckering motion is considered.[12]

The ^1H n.m.r. spectrum of the palladacyclobutan-3-one complex **(1a)**, measured at −50 °C in $CDCl_3$, showed the expected features for the illustrated static structure with two resonances at δ 3.14 and 2.84 for the methyl protons of the carboxymethyl groups and signals for the CH groups on palladium at δ 4.54 [d, $^3J(PH)$ 10.3 Hz] and 3.71 [t, $^3J(PH)$ 4.2 Hz]. This triplet may arise by both phosphorus nuclei coupling, by a similar magnitude, with the equatorial CH hydrogen atom of the ring since both phosphorus atoms are almost coplanar with the equatorial CH bond. Warming to room temperature caused reversible changes in these signals, the methyl resonances collapsing to a singlet at δ 2.95 and the CH protons collapsing to a doublet at δ 4.11 [$^3J(PH)$ 3.9 Hz]. These results are consistent with an inversion of the ring through a planar structure. The free energy of activation, $\Delta G^{\ddagger}_{T_c}$, calculated for this process from the coalescence temperature is 50.9 kJ mol^{-1}. The palladium complexes **(1b)**—**(1e)** exhibit similar temperature-dependent n.m.r. spectra; the free energies of activation for the exchange processes increase with the angle of puckering (Table 1).

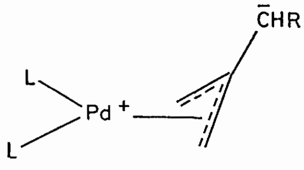
The magnitude of the barrier to inversion observed for the palladacyclobutan-3-one complexes is presumably a consequence of the palladium–carbon transannular interaction, which will be broken during inversion. Transannular platinum–carbon interactions may be of importance in skeletal isomerizations of platinacyclobutanes, although the ground



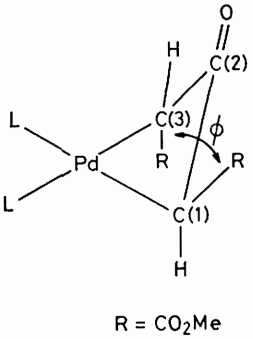
(1) a; L = PPh_3
b; L = $PMePh_2$
c; L = PMe_2Ph
d; L = $AsPh_3$
e; L_2= bipy
R = CO_2Me



(2) R = CO_2Me



(3) L = PPh_3



R = CO_2Me

Table 1. Structural data and values of the free energy of activation ($\Delta G^{\ddagger}_{T_c}$) for the barrier to inversion for some palladacyclobutan-3-one complexes.

	L = PPh_3	L = $AsPh_3$	L_2 = bipy
ϕ/°	54.0	52.7	51.3
Pd . . . C(2)/Å	2.402	2.386	2.374
av. Pd–C(1),–C(3)/Å	2.155	2.132	2.094
av. ring C–C/Å	1.48	1.45	1.47
C(2)=O/Å	1.23	1.24	1.24
$\Delta G^{\ddagger}_{T_c}$, inv./kJ mol^{-1}	50.9	44.4	40.4

state puckering of these rings is small, transannular platinum–carbon distances being in the range 2.6—2.7 Å.[13]

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References

1 R. J. Al-Essa, R. J. Puddephatt, P. J. Thompson, and C. F. H. Tipper, *J. Am. Chem. Soc.*, 1980, **102**, 7546.
2 C. P. Casey, D. M. Scheck, and A. J. Shusterman, *J. Am. Chem. Soc.*, 1979, **101**, 4233.
3 T. R. Howard, J. B. Lee, and R. H. Grubbs, *J. Am. Chem. Soc.*, 1980, **102**, 6876.
4 O. Eisenstein, R. Hoffman, and A. R. Rossi, *J. Am. Chem. Soc.*, 1981, **103**, 5582.
5 D. A. Clarke, R. D. W. Kemmitt, M. A. Mazid, M. D. Schilling, and D. R. Russell, *J. Chem. Soc., Chem. Commun.*, 1978, 744.
6 T. H. Tulip and D. L. Thorn, *J. Am. Chem. Soc.*, 1981, **103**, 2448.
7 T. Ukai, H. Kawazura, Y. Ishii, J. J. Bonnet, and J. A. Ibers, *J. Organomet. Chem.*, 1974, **65**, 253.
8 M. E. Kastner and W. R. Scheidt, *J. Organomet. Chem.*, 1978, **157**, 109.
9 W. P. Schaefer, R. Waltzman, and B. T. Huie, *J. Am. Chem. Soc.*, 1978, **100**, 5063.
10 A. Nishinaga, K. Nishizawa, Y. Nakayama, and T. Matsuura, *Tetrahedron Lett.*, 1977, 85.
11 D. J. Gordon, R. F. Fenske, T. N. Nanninga, and B. M. Trost, *J. Am. Chem. Soc.*, 1981, **103**, 5974.
12 R. J. Klinger, J. C. Huffman, and J. K. Kochi, *J. Organomet. Chem.*, 1981, **206**, C7.
13 R. J. Puddephatt, *Coord. Chem. Rev.*, 1980, **33**, 149.