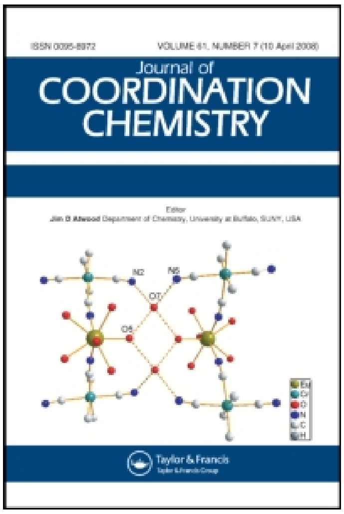

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

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**To cite this Article** Simpson, R. T. and Carty, A. J.(1973) 'STABILIZATION OF THE *cis* CONFIGURATION OF DIHALO BIS(TERTIARY PHOSPHINE) PALLADIUM(II) COMPLEXES BY PHOSPHINOACETYLENES', Journal of Coordination Chemistry, 2: 3, 207 — 209

**To link to this Article: DOI:** 10.1080/00958977308072973

**URL:** http://dx.doi.org/10.1080/00958977308072973

*J. Coord. Chem.*, 1973, Vol. 2, pp. 207–209

# STABILIZATION OF THE *cis* CONFIGURATION OF DIHALO BIS(TERTIARY PHOSPHINE) PALLADIUM(II) COMPLEXES BY PHOSPHINOACETYLENES

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(*Received in final form July* 11, 1972)

Although many complexes of the types *cis* and *trans* $PtX_2(PR_3)_2$ have been characterized[1] the more labile palladium analogues usually exist in the *trans* configuration. Indeed the only *cis* palladium complexes of monodentate phosphines which have been isolated pure in the solid state are $PdCl_2(Bu_2PhP)_2$,[2] $PdCl_2(Me_2PhP)_2$,[3,4] $PdCl_2(Et_2PhP)_2$[2] and $PdX_2(Me_3P)_2$ (X = Cl, Br).[5,6] Thus only one *cis* bromide and no *cis* iodide complexes are known. We have succeeded in preparing a series of *cis* complexes including several bromides by utilizing the phosphinoacetylenes $Ph_2PC{\equiv}CR$ (R = $CF_3$, *t*-Bu, Et, *i*-Pr) which have by virtue of the linear $-C{\equiv}C-R$ group a reduced steric requirement when compared to triaryl or alkyl diarylphosphines. These syntheses more than double the number of known *cis* bis(phosphine) palladium complexes and confirm indications from recent work[2,5,6] that steric effects may be of major importance in destabilizing the *cis* palladium isomers.

Reaction of $(PhCN)_2PdCl_2$ in $CH_2Cl_2$/EtOH with $Ph_2PC{\equiv}CR$ (R = $CF_3$, *t*-Bu, Et, *i*-Pr) gave immediate crystalline yellow precipitates of $PdCl_2(Ph_2PC{\equiv}CR)_2$. Recrystallization from $CH_2Cl_2$/EtOH afforded the pure lemon yellow *cis* compounds. There was no evidence (vide infra) for the more highly coloured *trans* species with any of the chlorides. Metathesis of $PdCl_2(Ph_2PC{\equiv}CR)_2$ with KBr or KI in acetone gave the bromo and iodo compounds (Table). The configuration of these compounds was established by far-infrared and Raman studies and confirmed by a single crystal X-Ray determination of *cis* $Pd(NCS)(SCN)(Ph_2PC{\equiv}CBu^t)_2$† prepared from $PdCl_2(Ph_2PC{\equiv}CBu^t)_2$ by metathesis.[7] ν(Pd–X) bands observed in the i.r. and Raman spectra are recorded in the Table. The i.r. spectra of *cis* $PdCl_2(Ph_2PC{\equiv}CBu^t)_2$ cis $PdBr_2(Ph_2PC{\equiv}CBu^t)_2$ and *trans* $PdI_2(Ph_2PC{\equiv}CBu^t)_2$ are shown in the figure. Cis isomers were readily identified by the

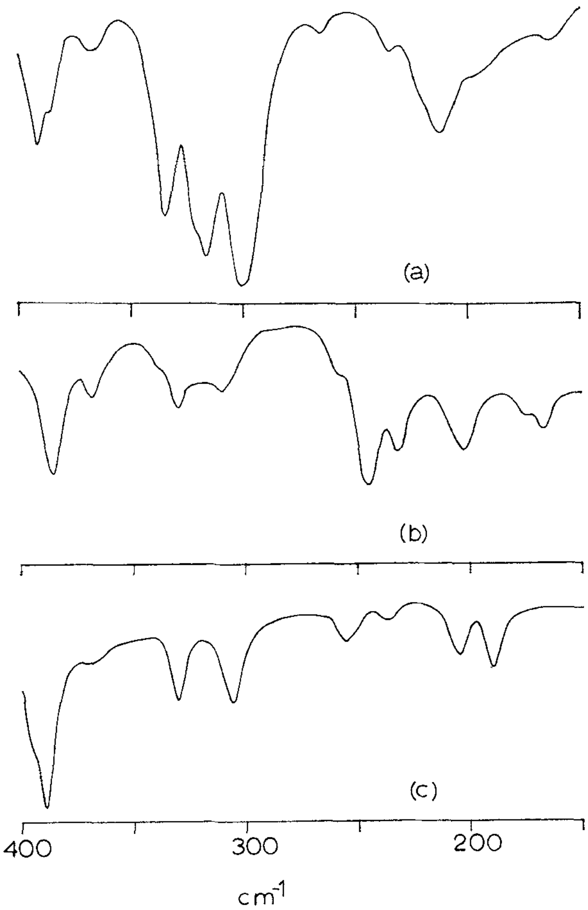

FIGURE 1 Far-infrared spectra (400-150 cm⁻¹) of (*a*) *cis* $PdCl_2(Ph_2PC{\equiv}CBu^t)_2$, (*b*) *cis* $PdBr_2(Ph_2PC{\equiv}CBu^t)_2$ and (*c*) *trans* $PdI_2(Ph_2PC{\equiv}CBu^t)_2$.

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† *cis* Pd(NCS) (SCN) $(Ph_2PC{\equiv}CBu^t)_2$ is the first known *cis* bis (phosphine) palladium thiocyanate complex.

presence of two strong, closely spaced $\nu$(Pd–X) bands coincident in the i.r. and Raman at lower frequency than the single $\nu(\text{Pd–X})_{as}$ i.r. band of *trans* compounds.[8] Furthermore the *cis* bromo complexes were lemon yellow whereas *trans* complexes are generally orange. As additional evidence for the *cis* configuration we prepared the complexes *cis* $PdCl_2(PhMePC{\equiv}CPh)_2$ *cis* $PdBr_2(PhMePC{\equiv}CPh)_2$ and *trans* $PdI_2(PhMePC{\equiv}CPh)_2$. The absence of virtual coupling[3] in the $^1$H *nmr* spectrum of the chloride (60 MHz$^{-1}$ $CDCl_3$; $\delta$ 7.5 m (phenyl) $\delta$ 2.3 *d* (methyl) $J_{P-H}$ 12.0 Hz) and the bromide ($\delta$ 7.5 m (phenyl) $\delta$ 2.4 d (methyl) $J_{P-H}$ 12.0 Hz) and the presence of virtual coupling in the iodide ($\delta$ 7.6 m (phenyl) $\delta$ 2.6 t (methyl) $J_{P-H}$ 4.0 Hz) confirmed the geometries assigned from the i.r. spectra.

Previous work[10] has indicated that the isomerizations *cis* → *trans* $PtCl_2(Et_3M)_2$(M = P, As, Sb) are accompanied by an endothermic enthaply change indicating a greater total bond energy in the *cis* isomers. Conversely, the entropy term favoured less highly solvated *trans* species. Although less important for $PtCl_2(Et_3M)_2$ due to the size of the platinum atom,[10] steric effects between bulky *cis* tertiary phosphine ligands may play a somewhat larger role in influencing the position of equilibrium for *cis* and *trans* $PdCl_2(R_3P)_2$ by reducing ΔH for the *cis* → *trans* isomerization process. Indeed steric crowding of *cis* phosphine ligands in

TABLE I

Palladium-halogen stretching frequencies in complexes[a, b]

| | $\nu$(Pd–X) (cm$^{-1}$) | | |
|---|---|---|---|
| Compound[c] | i.r. | Raman | Colour |
| *cis*-$PdCl_2(Ph_2PC{\equiv}CBu^t)_2$ | 300.0, 315.9 | 317, 301 | yellow |
| *cis*-$PdBr_2(Ph_2PC{\equiv}CBu^t)_2$ | 244.7, 231.3 | 247, 236 | yellow |
| *trans*-$PdI_2(Ph_2PC{\equiv}CBu^t)_2$ | 189.2 | | red |
| *cis*-$PdCl_2(Ph_2PC{\equiv}CEt)_2$ | 317.3, 293.0 | 316, 299 | yellow |
| *cis*-$PdBr_2(Ph_2PC{\equiv}CEt)_2$ | 235.5, 207.2 | | yellow |
| *trans*-$PdI_2(Ph_2PC{\equiv}CEt)_2$ | 189.9 | | red |
| *cis*-$PdCl_2(Ph_2PC{\equiv}CCF_3)_2$ | 318.6, 300.6 | 320, 304 | yellow |
| *trans*-$PdBr_2(Ph_2PC{\equiv}CCF_3)_2$ | 283.5 | 288[d] | orange |
| *trans*-$PdI_2(Ph_2PC{\equiv}CCF_3)_2$ | 192.7 | | red |
| *cis*-$PdCl_2(Ph_2PC{\equiv}CPr^i)_2$ | 330.1, 299(sh) 293.0[e] | 331, 301 | yellow |
| *cis*-$PdBr_2(Ph_2PC{\equiv}CPr^i)_2$ | 240.6, 208.0 | | yellow |
| *trans*-$PdI_2(Ph_2PC{\equiv}CPr^i)_2$ | 188.5 | | red |
| *cis*-$PdCl_2(PhMePC{\equiv}CPh)_2$ | 320.8, 300.0 | 318, 299 | yellow |
| *cis*-$PdBr_2(PhMePC{\equiv}CPh)_2$ | 249.8, 232.7 | | yellow |
| *trans*-$PdI_2(PhMePC{\equiv}CPh)_2$ | 196.0 | | red |

[a] i.r. spectra measured as nujol mulls between CsI and polyethylene plates on a P.E. 180 spectrometer. Raman spectra measured on solid samples using a Cary 81 spectrometer using Argon ion laser excitation. i.r. frequencies are accurate to $\pm 0{\cdot}5$ cm$^{-1}$. Raman frequencies are accurate to $\pm 1$ cm$^{-1}$.

[b] In view of the difficulties in assigning $\nu$(Pd-P) vibrations without metal isotopic substitution[8] no attempt was made to make these assignments.

[c] Satisfactory C and H analysis obtained for all compounds.

[d] in $CH_2Cl_2$

[e] These bands are all absent in the corresponding bromide and iodide complexes and are therefore assigned as $\nu$(Pd—Cl) modes. None of the bands are at high enough wavenumber for a *trans* isomer. The Raman spectrum exhibits only two bands due to $\nu$(Pd—Cl) however.

*cis* $PdCl_2(Me_2PhP)_2$[4] is apparently responsible for a P–Pd–P angle of 97·85° although there is as yet insufficient X-ray data available to assess the effect of the distortion on the Pd—P and Pd—Cl bond strengths.

The replacement of R of $Ph_2RP$ (R = alkyl, aryl) by $-C{\equiv}CR$ effectively reduces the steric demand of these phosphines since there are no $\alpha$ or $\beta$ hydrogen atoms on the $-C{\equiv}C-R$ group. Consistent with this,† the ligands $R_2PC{\equiv}CR'$ readily displace three molecules of CO from $Ni(CO)_4$.[11] In addition the X-ray structure determination of $Pd(NCS)(SCN)(Ph_2PC{\equiv}CBu^t)_2$ shows that the $-C{\equiv}CBu^t$ groups straddle one another to minimize contacts between phenyl groups on different phosphorus atoms.[7] These results indicate the possible importance of steric effects in *cis* palladium complexes. The synthesis of other phosphine ligands with minimal steric demands is now being undertaken.

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† The degree of substitution of $Ni(CO)_4$ by $R_3P$ is known to be dependent mainly on the steric properties of the ligands.[12]

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