Journal of Organometallic Chemistry, 379 (1989) 177–185
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
JOM 20330

Insertions of diphenylacetylene into cyclopalladated compounds. Crystal structure of $[\mathrm{P\overline{d\{(PhC{=}CPh)_2C_6H_4CH_2N}{=}CH(2,6\text{-}C_6H_3Cl_2)\}Br}]$

Joan Albert, Jaume Granell, Joaquim Sales

Departament de Química Inorgànica, Universitat de Barcelona, Diagonal 647, 08028 Barcelona (Spain)

and Xavier Solans

Departament de Cristal.lografia, Mineralogia i Dipòsits Minerals, Universitat de Barcelona, Martí i Franquès s/n 08028 Barcelona (Spain)

(Received July 21st, 1989)

Abstract

The reaction between $[\mathrm{P\overline{d\{C_6H_4CH_2N}{=}CH(2,6\text{-}C_6H_3Cl_2)\}Br}]_2$ and PhC≡CPh gives the bis-insertion compound $[\mathrm{P\overline{d\{(PhC{=}CPh)_2C_6H_4CH_2N}{=}CH(2,6\text{-}C_6H_3Cl_2)\}}$ Br] in good yield. This compound crystallizes in the monoclinic space group $P2_1/a$, with a 18.757(3), b 15.678(3), c, 12.150(2) Å β 92.83(2)° and $Z = 4$; $R = 0.063$ for 2076 reflections. The palladium atom is coordinated to Br, N, C(18), and the centre of the C(15)–C(16) double bond in a distorted square-planar geometry.

Introduction

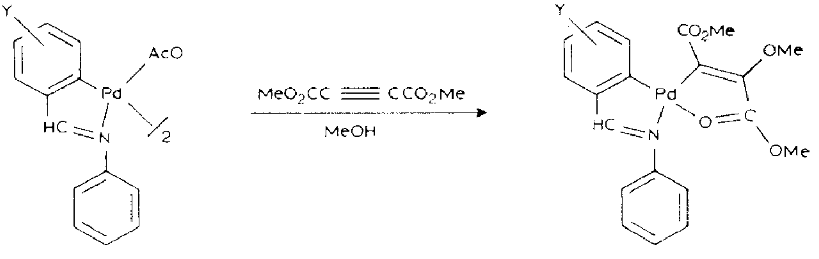
Cyclopalladated compounds are valuable intermediates for regioselective organic synthesis. Carbonylation, vinylation, alkylation, and halogenation reactions of these compounds have been much studied [1]. Recently, increasing attention has been paid to the insertion of alkynes into the Pd–C bonds. Insertion of symmetric and asymmetric alkynes into several five- [2,3] and six-membered [4] cyclopalladated complexes with different *N*-donor ligands, and also into a few *S*-donor [5] and *O*-donor [6] derivatives have been reported. Mono-, bis- and tris-insertions of alkynes have been observed, with formation of seven- and nine-membered cyclometallated complexes, but usually depalladation occurs and heterocyclic organic molecules are formed, some of them closely related to certain natural products.

It is accepted that insertion of alkynes into the Pd–C bonds takes place after the alkyne coordination to the metal. Thus cationic species with solvent molecules as ligands react more easily with alkynes.

Although several cyclopalladated derivatives of Schiff bases are known, their reactivity with alkynes has been scarcely studied. Pregosin and Albinati [7] observed

0022-328X/89/$03.50

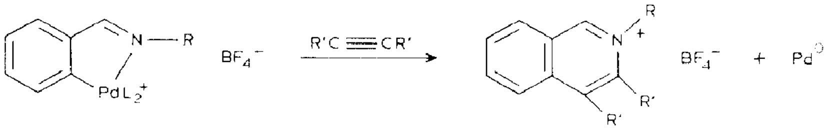
no insertion of $MeO_2C-C{\equiv}C-CO_2Me$ in the Pd–C bond of cyclopalladated *N*-benzylidenaniline derivatives, and compound **2** (eq. 1) was formed by attack of



(1)

(**1**) (**2**)

OMe on the alkyne coordinated to the metal. Unactivated alkynes, such as $PhC{\equiv}CPh$, did not react Heck et al. [3] have described the preparation of isoquinolinium salts (**4**) from the very reactive cationic cyclometallated benzaldimines (**3**) and alkynes (eq. 2).



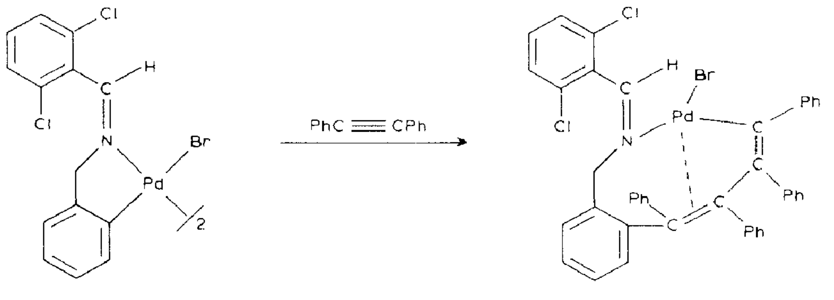
(2)

(**3**) (**4**)

Recently we have obtained cyclometallated derivatives of *N*-benzylidenbenzylamines in which the iminic doble bond C=N is not part of the metallacycle (the so-called *exo* structure) [8]. These *exo* derivatives are more reactive than the analogous *endo* complexes. Thus, the action of PPh_3 in excess on compound **5** caused cleavage of the Pd–N bond to give $[PdBr\{C_6H_4CH_2N{=}CH(2,6\text{-}C_6H_3Cl_2)\}(PPh_3)_2]$. However for the *endo* derivatives $[PdBr(p\text{-}RC_6H_4CH{=}NCH_2C_6H_5)]_2$, only the cyclometallated compounds $[PdBr(p\text{-}RC_6H_4CH{=}NCH_2C_6H_5)(PPh_3)]$ were obtained [9]. Ligand exchange reactions between cyclopalladated compounds and free *N*-donor ligands also reveal the greater reactivity of the *exo* derivatives [10]. It thus seemed likely that *exo* cyclometallated derivatives of *N*-benzylidenbenzylamines would readily undergo coordination of alkynes, and hence the insertion into the Pd–C bond.

Results and discussion

The action of $PhC{\equiv}CPh$ on the complex **5** gives the nine-membered cyclometallated compound **6** resulting from insertion of two alkyne molecules (eq. 3).



(3)

(**5**) (**6**)

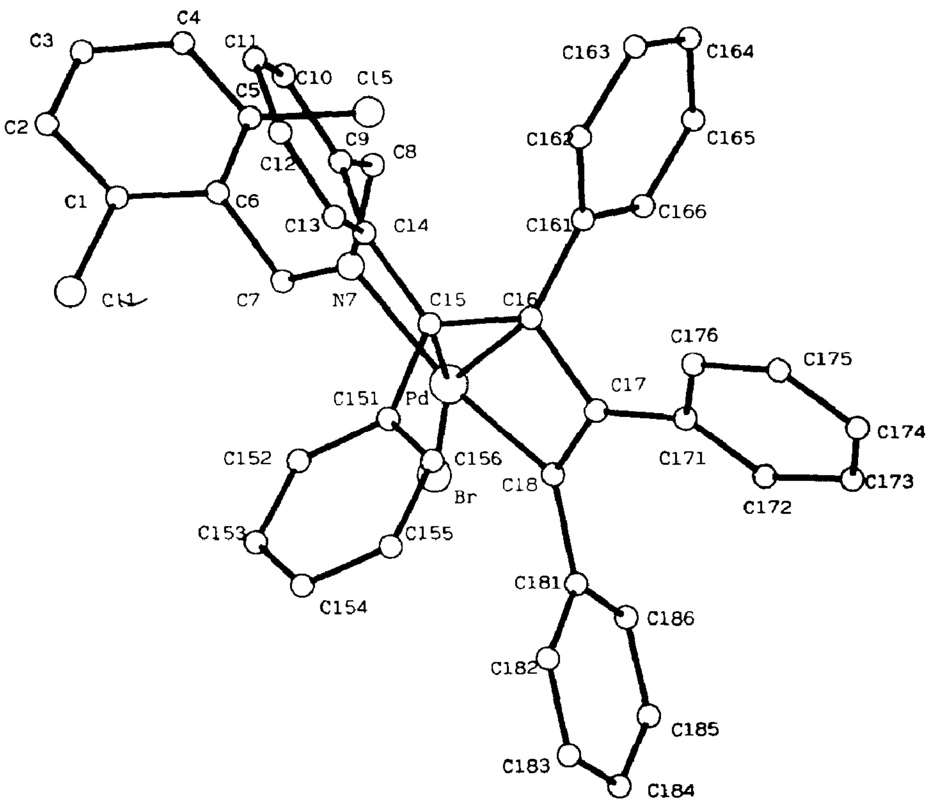


Fig. 1. Molecular structure of $[\overline{\mathrm{Pd}\{(\mathrm{PhC{=}CPh})_2\mathrm{C_6H_4CH_2N}}{=}\mathrm{CH}(2,6\text{-}\mathrm{C_6H_3Cl_2})\}\mathrm{Br}]$.

The NMR spectrum of **6** shows the methinic proton signal at $\delta = 9.1$, i.e. 0.5 ppm downfield from that for the free imine. This shift is in agreement with the proximity of methinic hydrogen to the palladium atom which arises from the *syn* form adopted by the metallated imine (see X-ray structure, Fig. 1). The methylenic proton appears as an AB quartet at $\delta = 3.95$ ppm. A broad multiplet is observed for the aromatic hydrogens at $\delta = 7.25$ ppm.

The molecular structure of **6** has been determined (Fig. 1). Bond distances and angles as well as non-hydrogen atomic coordinates, are shown in Tables 1 and 2, respectively.

The palladium atom is bonded to Br, N(7), C(18), and X the middle of the C(15)–C(16) double bond; in a distorted square-planar geometry. The deviations from the mean plane are Pd: −0.051Å; C(18): 0.052Å; Br: −0.017Å; N(7): 0.044Å; X: −0.027A. The Pd–Br, Pd–N(7) and Pd–C(18) distances and related angles are similar to those in five-membered cyclopalladated compounds [11]. The Pd–C(15) and Pd–C(16) lengths are slightly different from one another, and the C(15)PdC(16) angle is 36.61°. Furthermore the C(15)–C(16) bond is slightly longer than the C(17)–C(18) bond owing to coordination to the palladium atom. The C(15)–C(16) double bond forms a dihedral angle of 67.7° with the coordination plane of the complex. The torsion dihedral angle C(6)C(7)NC(8) is 0.00°, reflecting the *syn* form adopted by the imine ligand. An isomerization to the *anti* form would give rise to strong steric interactions between the 2,6-$C_6H_3Cl_2$ group and the palladium atom.

Table 1

Bond distances (Å) and angles (°) for compound **6**

Pd–X	2.105(15)
Br–Pd	2.445(2)
N(7)–Pd	2.133(13)
C(15)–Pd	2.258(13)
C(16)–Pd	2.215(15)
C(18)–Pd	2.004(14)
C(1)–Cl(1)	1.727(27)
C(5)–Cl(2)	1.655(30)
C(2)–C(1)	1.413(48)
C(6)–C(1)	1.376(39)
C(3)–C(2)	1.279(58)
C(4)–C(3)	1.410(56)
C(5)–C(4)	1.404(48)
C(6)–C(5)	1.334(39)
C(7)–C(6)	1.527(28)
N(7)–C(7)	1.296(22)
C(8)–N(7)	1.474(20)
C(9)–C(8)	1.492(22)
C(10)–C(9)	1.401(24)
C(14)–C(9)	1.376(23)
C(11)–C(10)	1.414(28)
C(12)–C(11)	1.380(28)
C(13)–C(12)	1.373(26)
C(14)–C(13)	1.423(23)
C(15)–C(14)	1.493(22)
C(16)–C(15)	1.404(24)
C(151)–C(15)	1.495(22)
C(17)–C(16)	1.499(23)
C(161)–C(16)	1.485(22)
C(18)–C(17)	1.335(21)
C(171)–C(17)	1.452(23)
C(181)–C(18)	1.488(22)
C(152)–C(151)	1.381(25)
C(156)–C(151)	1.412(26)
C(153)–C(152)	1.338(32)
C(154)–C(153)	1.423(37)
C(155)–C(154)	1.378(36)
C(156)–C(155)	1.402(31)
C(162)–C(161)	1.414(25)
C(166)–C(161)	1.402(25)
C(163)–C(162)	1.423(31)
C(164)–C(163)	1.377(34)
C(165)–C(164)	1.363(35)
C(166)–C(165)	1.335(29)
C(172)–C(171)	1.374(25)
C(176)–C(171)	1.367(23)
C(173)–C(172)	1.405(30)
C(174)–C(173)	1.421(34)
C(175)–C(174)	1.338(32)
C(176)–C(175)	1.403(27)
C(182)–C(181)	1.380(29)
C(186)–C(181)	1.406(27)
C(183)–C(182)	1.312(34)
C(184)–C(183)	1.345(41)
C(185)–C(184)	1.350(42)
C(186)–C(185)	1.339(35)

Table 1 (continued)

Br–Pd–X	170.9(8)
N(7)–Pd–X	96.8(9)
C(15)–Pd–X	18.1(7)
C(16)–Pd–X	18.4(8)
C(18)–Pd–X	74.4(9)
N(7)–Pd–Br	92.1(3)
C(15)–Pd–Br	165.8(4)
C(15)–Pd–N(7)	88.3(5)
C(16)–Pd–Br	154.8(5)
C(16)–Pd–N(7)	105.1(5)
C(16)–Pd–C(15)	36.6(6)
C(18)–Pd–Br	96.5(4)
C(18)–Pd–N(7)	169.7(5)
C(18)–Pd–C(15)	84.7(6)
C(18)–Pd–C(16)	65.0(6)
C(2)–C(1)–Cl(1)	116.3(26)
C(6)–C(1)–Cl(1)	122.9(23)
C(6)–C(1)–C(2)	120.8(26)
C(3)–C(2)–C(1)	116.9(34)
C(4)–C(3)–C(2)	125.6(39)
C(5)–C(4)–C(3)	115.5(34)
C(4)–C(5)–Cl(2)	117.7(25)
C(6)–C(5)–Cl(2)	121.4(22)
C(6)–C(5)–C(4)	120.9(28)
C(5)–C(6)–C(1)	120.1(24)
C(7)–C(6)–C(1)	113.6(21)
C(7)–C(6)–C(5)	126.3(21)
N(7)–C(7)–C(6)	121.3(15)
C(7)–N(7)–Pd	122.5(11)
C(8)–N(7)–Pd	113.9(9)
C(8)–N(7)–C(7)	123.5(13)
C(9)–C(8)–N(7)	111.0(13)
C(10)–C(9)–C(8)	117.0(15)
C(14)–C(9)–C(8)	125.0(14)
C(14)–C(9)–C(10)	117.9(15)
C(11)–C(10)–C(9)	122.3(17)
C(12)–C(11)–C(10)	119.3(17)
C(13)–C(12)–C(11)	118.6(17)
C(14)–C(13)–C(12)	122.6(17)
C(13)–C(14)–C(9)	119.3(15)
C(15)–C(14)–C(9)	125.9(14)
C(15)–C(14)–C(13)	114.4(14)
C(14)–C(15)–Pd	118.2(10)
C(16)–C(15)–Pd	70.0(8)
C(16)–C(15)–C(14)	123.2(13)
C(151)–C(15)–Pd	98.6(9)
C(151)–C(15)–C(14)	113.4(13)
C(151)–C(15)–C(16)	120.9(14)
C(15)–C(16)–Pd	73.4(9)
C(17)–C(16)–Pd	86.8(9)
C(17)–C(16)–C(15)	120.9(12)
C(161)–C(16)–Pd	116.8(11)
C(161)–C(16)–C(15)	122.7(15)
C(161)–C(16)–C(17)	116.1(15)
C(18)–C(17)–C(16)	106.5(13)
C(171)–C(17)–C(16)	121.1(13)

Table 1 (continued)

C(171)–C(17)–C(18)	132.4(14)
C(17)–C(18)–Pd	100.6(10)
C(181)–C(18)–Pd	130.6(11)
C(181)–C(18)–C(17)	128.7(14)
C(152)–C(151)–C(15)	120.7(15)
C(156)–C(151)–C(15)	122.2(15)
C(156)–C(151)–C(152)	116.7(16)
C(153)–C(152)–C(151)	123.0(19)
C(154)–C(153)–C(152)	119.5(21)
C(155)–C(154)–C(153)	120.9(22)
C(156)–C(155)–C(154)	117.1(21)
C(155)–C(156)–C(151)	122.6(18)
C(162)–C(161)–C(16)	122.9(16)
C(166)–C(161)–C(16)	119.6(16)
C(166)–C(161)–C(162)	117.4(16)
C(163)–C(162)–C(161)	117.9(17)
C(164)–C(163)–C(162)	121.1(21)
C(165)–C(164)–C(163)	119.7(21)
C(166)–C(165)–C(164)	120.5(20)
C(165)–C(166)–C(161)	123.3(18)
C(172)–C(171)–C(17)	118.9(15)
C(176)–C(171)–C(17)	120.6(15)
C(176)–C(171)–C(172)	120.4(16)
C(173)–C(172)–C(171)	117.2(17)
C(174)–C(173)–C(172)	121.9(19)
C(175)–C(174)–C(173)	118.9(21)
C(176)–C(175)–C(174)	119.3(17)
C(175)–C(176)–C(171)	122.2(16)
C(182)–C(181)–C(18)	121.4(16)
C(186)–C(181)–C(18)	121.9(17)
C(186)–C(181)–C(182)	116.8(18)
C(183)–C(182)–C(181)	122.0(21)
C(184)–C(183)–C(182)	120.9(26)
C(185)–C(184)–C(183)	119.4(26)
C(186)–C(185)–C(184)	121.6(23)
C(185)–C(186)–C(181)	119.2(21)

This 2,6-$C_6H_3Cl_2$ group forms a dihedral angle of 71.81° with the iminic moiety. The phenylic substituents on the double bond C(17)–C(18) are *cis* to one another, and those of the C(15)–C(16) *trans* to one another; this arrangement results in less steric hindrance with and between the remaining ligands.

The nine-membered metallocycle can be seen as formed by two distorted planar rings with a dihedral angle of 141.45° (Table 3).

The molecular structure of **6** is similar to those reported for $[Pd\{(CR{=}CR)_2C_6H_4CH_2NMe_2\}X]$ (X = Cl, Br) obtained by insertion of disubstituted alkynes RC≡CR′ (R,R′ = Me or Ph) into the cyclopalladated complex $[PdX(C_6H_4CH_2NMe_2)]_2$ [12]. The differences observed can be attributed to the asymmetric character of the inserted alkynes.

Our results are very different from those reported by Pregosin [7] and Heck [3] for analogous cyclometallated derivatives of *N*-benzylidenbenzylamines, with *endo*

Table 2

Final atomic coordinates ($\times 10^4$) for compound **6**

Atom	*x*	*y*	*z*
Pd	35487(7)	24665(9)	25009(10)
Br	2267(1)	2216(2)	2210(2)
Cl(1)	3098(4)	2266(5)	6665(5)
Cl(2)	2369(4)	5002(5)	4251(7)
C(1)	2827(11)	3314(17)	6520(28)
C(2)	2697(17)	3757(26)	7503(28)
C(3)	2520(18)	4543(27)	7410(35)
C(4)	2400(16)	4988(26)	6410(30)
C(5)	2522(13)	4521(19)	5452(23)
C(6)	2728(10)	3707(16)	5511(17)
C(7)	2851(10)	3118(11)	4537(14)
N(7)	3397(6)	3215(8)	3936(11)
C(8)	3938(8)	3888(10)	4128(13)
C(9)	4636(9)	3517(11)	4527(13)
C(10)	4981(12)	3904(11)	5447(15)
C(11)	5666(11)	3646(13)	5858(15)
C(12)	6002(10)	2976(13)	5358(16)
C(13)	5662(9)	2590(12)	4463(14)
C(14)	4974(8)	2847(10)	4041(13)
C(15)	4721(7)	2397(9)	3011(14)
C(16)	4629(8)	2806(8)	1986(15)
C(17)	4454(8)	2305(9)	956(13)
C(18)	3839(8)	1904(9)	1111(12)
C(151)	4794(9)	1449(10)	3083(13)
C(152)	4405(10)	986(12)	3812(15)
C(153)	4477(12)	143(17)	3946(19)
C(154)	4999(16)	−303(14)	3359(20)
C(155)	5417(13)	116(16)	2632(17)
C(156)	5316(11)	998(12)	2518(15)
C(161)	4779(10)	3727(11)	1833(14)
C(162)	5422(9)	4118(13)	2223(13)
C(163)	5516(13)	5000(15)	1995(17)
C(164)	4993(16)	5462(13)	1428(20)
C(165)	4383(13)	5065(15)	1044(16)
C(166)	4286(10)	4234(12)	1225(14)
C(171)	4926(9)	2313(9)	43(14)
C(172)	4639(10)	2189(10)	−1007(16)
C(173)	5108(13)	2228(11)	−1872(17)
C(174)	5854(13)	2350(12)	−1675(20)
C(175)	6110(9)	2479(13)	−641(18)
C(176)	5638(9)	2475(10)	219(14)
C(181)	3492(10)	1209(12)	444(13)
C(182)	3755(12)	387(14)	479(16)
C(183)	3463(16)	−228(17)	−120(22)
C(184)	2886(17)	−80(19)	−795(23)
C(185)	2608(12)	714(19)	−859(21)
C(186)	2877(11)	1354(14)	−239(18)

metallocycles, but are very similar to those obtained by Pfeffer et al. [12] for the dimethylbenzylamine derivatives, in keeping with the greater lability of the Pd–N bonds.

Table 3

Planes and deviations (Å) for the metallocycle

Ring Pd,N(7),C(8),C(9),C(14),C(15),C(16)

$0.1986x + 0.6810y - 0.7049z = 1.9390$

Pd: 0.105; N: −0.391; C(8): 0.399; C(9): −0.034
C(14): −0.185; C(15): 0.106

Ring Pd,C(16),C(17),C(18)

$0.4138x - 0.7754y + 0.4770z = 1.0784$

Pd: −0.033; C(16): 0.046, C(17): −0.070; C(18): 0.058

Experimental

NMR spectra were obtained on Bruker WP80 SY spectrometer in $CDCl_3$, chemical shifts (δ/ppm) with internal TMS as reference. IR spectra (KBr discs) were recorded on a Perkin–Elmer 1330 spectrometer. Microanalyses were performed by the Institut de Química Bo-Orgànica de Barcelona (CSIC).

Crystal data

$C_{42}H_{32}NCl_2BrPd$. FW = 807.94, monoclinic, $a = 18.757(3)$, $b = 15.678(3)$, $c = 12.150(2)$ Å, $\beta = 92.83(2)°$, $V = 3569(1)$ Å^3, $P2_1/a$, $D_x = 1.503$ g cm^{-3}, $Z = 4$, $F(000) = 1624$, $\lambda(\text{Mo-}K_\alpha) = 0.71069$ Å, $\mu(\text{Mo-}K_\alpha) = 18.77$ cm^{-1} 288 K.

Data collection

A rectangular crystal (0.2 × 0.2 × 0.1 mm) was selected and mounted on a Philips PW-1100 four circle diffractometer. Unit cell parameters were determined from 25 reflections ($4 \leq \theta \leq 12°$) and refined by least-squares methods. Intensities were collected with graphite monochromatized Mo-K_α radiation by the ω-scan technique, with scan width 0.8° and scan speed 0.03° s^{-1}. 2432 reflections were measured in the range $224 < \theta < 25°$; 2076 with $I > 2.5\sigma(I)$ were regarded as observed. Three standard reflections measured every 2 h showed no significant intensity decay. Lorentz-polarization but no absorption corrections were made.

Structure solution and refinement

The structure was solved by direct methods with the MULTAN system of computer programs [13] and refined by full-matrix least-squares with the SHELX76 program [14]. The function minimized was $\Sigma w \| F_o | - | F_c \|$, were $w = (\sigma^2(F_o) + 0.008 | F_o |)^{-1}$. f, f' and f'' were taken from International Tables for X-ray Crystallography [15]. The H atoms were placed at calculated positions and refined with an overall isotopic thermal parameter. The remaining atoms were refined anisotrapically. The final R was 0.063 ($wR = 0.064$) for all observed reflections. Max. shift/e.s.d. = −0.1 in U_{12} of C(166). Max. peak in final difference synthesis 0.4 eA^{-3}. Tables of thermal parameters and final structure factors are available from the authors.

Materials and syntheses

Compound **5** was made by treatment of 2,6-$C_6H_3Cl_2CH{=}NCH_2C_6H_5$ with $Pd(AcO)_2$ in refluxing acetic acid followed by replacement of the AcO^- group by Br^- by use of LiBr in ethanol.

Compound **6** was obtained from a mixture of **5** (0.18 g, 0.2 mmol) and PhC≡CPh (0.14 g ,0.8 mmol) in chloroform (25 cm^3). The mixture was refluxed for 18 h. The solution was filtered and then evaporated to dryness in vacuo. The resulting solid was purified by column chromatography on SiO_2 with chloroform as the eluent. The yield was 65%. Anal. Found: C, 63.7; H, 4.0; N, 1.7. $C_{42}H_{32}NCl_2BrPd$ calc: C, 63.65; H, 3.95; N, 1.72%.

Acknowledgement

We thank the CAICYT (PB86-0575) for financial support.

References

1 A.D. Ryabov, Synthesis, (1985) 233.

2 F. Maassarani, M. Pfeffer and G. Le Borgne, Organometallics, 6 (1987) 2029. F. Maassarani, M. Pfeffer and G. van Koten, Organometallics, 8 (1989) 871.

3 G. Wu, A.L. Rheingold, S.J. Geib and R.F. Heck, Organometallics, 6 (1987) 1941. G. Wu, S.J. Geib, A.L. Rheingold and R.F. Heck, J. Org. Chem., 53 (1988) 3238.

4 F. Maassarani, M. Pfeffer and G. Le Borgne, Organometallics, 6 (1987) 2043. J. Dupont, M. Pfeffer, J.C. Daran and J. Gouleon, J. Chem. Soc., Dalton Trans., (1988) 2421.

5 J. Dupont and M. Pfeffer, J. Organomet. Chem., 321 (1987) C13. J. Dupont, M. Pfeffer, M.A. Rotteveel, A. Decian and J. Fischer, Organometallics, 8 (1989) 1116.

6 H. Ossor, M. Pfeffer, J.T. Jastrzebski and C.H. Stam, Inorg. Chem., 26 (1987) 1169.

7 A. Albinati, P.S. Pregosin and R. Rüedi, Helv. Chim. Acta, 68 (1985) 2046.

8 J. Albert, J. Granell and J. Sales, submitted for publication.

9 J. Albert, J. Granell and J. Sales, J. Organomet. Chem., 273 (1984) 393.

10 R.M. Ceder, M. Gomez and J. Sales, J. Organomet. Chem., 361 (1989) 391.

11 P.W. Clark, S.F. Dyke, G. Smith and C.H.L. Kennard, J. Organomet. Chem., 330 (1987) 473.

12 A. Bahosoun, J. Dehand, M. Pfeffer, M. Zinisius, S.E. Bouard and G. Le Borgne, J. Chem. Soc., Dalton Trans., (1979) 547.

13 P. Main, S.E. Fiske, S.L. Hull, L. Lessinger, G. Germain, J.P. Declerq and M.M. Woofson, MULTAN, an automatic system of computer programs for crystal structure determination from X-Ray difraction data, University of York, University of Louvain, Belgium 1984.

14 G.M. Sheldrick, SHELX 76, A computer program for crystal structure determination, University of Cambridge, 1976.

15 International Tables for X-Ray Crystallography, Kynoch Press, Birmingham, 1974, Vol. 4, pp. 99, 100, 149.