Journal of Organometallic Chemistry, 465 (1994) 289–296

JOM 23915

Phosphine-nitrile ligands: the molecular structure of *cis*-2-diphenylphosphino-1-cyanocyclopentane and studies of the donor/acceptor properties of this and related ligands

E.J. Fredericks [a], M.J. Gindling [a], L.C. Kroll [b] and B.N. Storhoff [a]

[a] *Department of Chemistry, Ball State University, Muncie, IN 47306 (USA)*
[b] *Department of Chemistry, Taylor University, Upland, IN 46989 (USA)*

(Received April 6, 1993; in revised from May 24, 1993)

Abstract

The *cis* and *trans* isomers of the previously reported 2-diphenylphosphino-1-cyanocyclo-pentane and -cyclohexane have been separated, and three of the four isomers have been obtained (both isomers of the former and one of the latter) as pure samples. An X-ray study of the $Ph_2PC_5H_8CN$ isomer with the more-shielded ^{31}P chemical shift proved it to be the *cis* isomer. A prominent feature observed for the structure is that the CN group is directed toward the phosphorus lone pair. Van der Waals and molecular mechanics calculations have suggested that the corresponding *trans* isomer has a structure in which the CN group is in general directed away from the phosphorus lone pair. Cone angle calculations based on the X-ray structure and calculated geometries of both *cis* and *trans* $Ph_2C_5H_8CN$ as well as the analogous $Ph_2C_5H_8(R)$ (R = H, CH_3) have provided values between 150° and 173° with the *cis* isomers having larger angles than the *trans*. Nonaqueous titrations have been used to determine pK_a values for the three cycloalkane-nitrile phosphines, and values between 2.44 and 2.52 have been obtained. IR and NMR studies of the $Ni(CO)_3L$ complexes of these three ligands have been completed, and the results indicate that these ligands are similar in effect to $PhP(OR)_2$. Both Pd^{II} and Pt^{II} complexes (all *trans* geometries) of these ligands have been obtained, and the P–N chelates (Pd) of the corresponding methyl imino ethers (from *trans* $Ph_2C_5H_8CN$ and $Ph_2PC_6H_{10}CN$) have also been isolated.

Key words: Phosphine-nitrile ligands; Nickel; Palladium; Platinum; Hindered (bulky) ligands; Molecular mechanics

1. Introduction

The chemical characteristics of phosphines have continued to be the subject of many theoretical and experimental studies [1] since the pioneering work by Tolman [2] to define and quantitate the steric and electronic properties of these widely used molecules. One of the driving forces behind this interest is the goal of understanding the subtle factors associated with processes such as enantioselective hydrogenation reactions catalyzed by phosphine complexes.

Recently we reported that Michael-like additions under mild conditions of diphenylphosphine, Ph_2PH, to 1-cyanocyclopentene, 1-cyanocyclohexene and 4-t-butyl-1-cyanocyclohexene provided good yields of mixtures of the corresponding *cis* and *trans* isomers of 2-diphenylphosphino-1-cyanocycloalkanes [3]. Our interest in further characterizing these phosphines arose from several observations. An examination of CPK models of these systems led to the conclusion that these and related ligands could have large cone angles. Also, focusing on the nitrile part of these systems, as a group it not only has interesting ligands properties [4], but also it has well-established reactivity patterns which make it a precusor for many other functionalities which could be used either as additional donor sites or as groups to tailor the cone angle and/or the electronic nature of the phosphine. In short, the many obtainable cycloalkane ring sizes, isomer possibilities, and cycloalkane substituent choices suggest that this combination can form the basis for versatile ligand systems.

Here we report procedures for separating and purifying three of the four *cis–trans* isomers of $Ph_2PC_5H_8$-CN and $Ph_2PC_6H_{10}CN$, the results from an X-ray crystallographic study of *cis*-$Ph_2PC_5H_8CN$, and calcu-

---

Correspondence to: Professor B.N. Storhoff.

0022-328X/94/$7.00
SSDI 0022-328X(93)23915-K

TABLE 1. pK_a values along with shifts in CO carbon ^{13}C NMR resonances and A_1 ν(CO) IR bands for Ni(CO)$_3$L complexes

Phosphine	pK_a	$\Delta\delta$ ^{13}C[a] (ppm)	ν(CO) values[b] (cm^{-1})
cis-$Ph_2C_5H_8CN$	2.44	4.23	2070.9
trans-$Ph_2C_5H_8CN$	2.52	4.26	2070.4
$Ph_2C_6H_{10}CN$	2.45	4.18	2070.2
$Ph_2PCH_2CH(CH_3)CN$	2.34	3.83	2071.6
$Ph_2PCH_2CH_2CN$	2.21	0.66	2072.0

[a] Downfield from Ni(CO)$_4$. [b] Ni(CO)$_3$PPh$_3$ (2068.9 cm^{-1}), ref. 2a.

lation-based predictions of structures and cone angles for these three compounds. In addition, the syntheses and spectroscopic results from selected studies of complexes of these ligands along with previously reported acyclic analogues 3-diphenylphosphinopropionitrile ($Ph_2PCH_2CH_2CN$) 3-diphenylphosphino-2-methylpropionitrile ($Ph_2PCH_2CH(CH_3)CN$) [5] with Ni^0, Pt^{II} and Pd^{II} will be presented.

2. Experimental section

2.1. Materials and instruments

$PdCl_2$, K_2PtCl_4 and Ni(CO)$_4$ were obtained from Aldrich, Fisher Scientific and Strem, respectively. Except as noted below, solvents were used as obtained from the chemical stores in our department. The phosphines $Ph_2PC_5H_8CN$ [3], $Ph_2PC_6H_{10}CN$ [3], $Ph_2PCH_2CH(CH_3)CN$ [5] and $Ph_2PCH_2CH_2CN$ [5] were obtained as described previously. IR and NMR spectra (see Tables 1 and 2) were recorded on Nicolet 5ZDX and Varian Gemini-200 instruments, respectively. The 5ZDX IR instrument was calibrated with solutions of Ni(CO)$_3$PPh$_3$ for which the A_1 CO stretching band has been reported to be 2068.9 cm^{-1} [2a]. Elemental analysis (see Table 3) were carried out by Midwest Microlab Ltd., Indianapolis, IN. Molecular weights were obtained by using a Hitachi Perkin Elmer 115 molecular weight apparatus. A Fisher model 395 syringe pump was used to deliver the perchloric acid for the titrations. The Molecular Structure Center (Indiana University, Bloomington, IN, 47405) carried out the X-ray analysis.

TABLE 2. Selected spectroscopic data

Compound[a]	δ ^{31}P	ν(CN)
(L1)$_2$PdCl$_2$[b]	28.45, 28.42	2225
(L2)$_2$PdCl$_2$[b]	20.57 20.48	2225
(L3)$_2$PdCl$_2$	25.0 25.3	2225
(L3)$_2$PtCl$_2$[c]	19.8	2220
(L1·MeOH)PdCl$_2$·CH$_2$Cl$_2$	31.3	1628
(L3·MeOH)PdCl$_2$	30.5	1628
L1Ni(CO)$_3$	40.0	
L2Ni(CO)$_3$	30.8	
L3Ni(CO)$_3$	34.1	

[a] L1, L2 and L3 are *trans*-$Ph_2C_5H_8CN$, *cis*-$Ph_2C_5H_8CN$ and the single pure isomer of $Ph_2C_6H_{10}CN$, respectively. L1·MeOH and L3·MeOH are the methyl imino ethers (imidates) of L1 and L3, respectively. [b] ν(PdCl) bands were observed at 355 cm^{-1}. [c] J(PtP) = 2524 Hz.

TABLE 3. Analytical and molecular weight data

Compound[a]	Analyses (Found (calcd.) (%))				Mol. wt.
	C	H	N	Cl	(g/mol)
(L1)$_2$PdCl$_2$	58.60	4.95	3.53	9.67	–
	(58.75)	(4.93)	(3.81)	(9.63)	(736)
(L2)$_2$PdCl$_2$	58.63	4.95	3.91	9.75	–
	(58.75)	(4.93)	(3.81)	(9.63)	(736)
(L3)$_2$PdCl$_2$	59.35	5.33	3.58	–	810
	(59.74)	(5.28)	(3.67)	(9.28)	(762)
(L3)$_2$PtCl$_2$	53.86	5.02	3.21	8.80	880
	(53.53)	(4.73)	(3.29)	(8.32)	(853)
(L1·MeOH)PdCl$_2$ ·CH$_2$Cl$_2$	41.87	4.29	2.46	24.21	–
	(41.88)	(4.22)	(2.44)	(24.72)	(489)
(L3·MeOH)PdCl$_2$	47.55	4.90	2.98	–	507
	(47.79)	(4.81)	(2.79)	(14.11)	(503)

[a] L1, L2 and L3 are *trans*-$Ph_2C_5H_8CN$, *cis*-$Ph_2C_5H_8CN$ and the single pure isomer of $Ph_2C_6H_{10}CN$, respectively. L1·MeOH and L3·MeOH are the methyl imino ethers (imidates) of L1 and L3, respectively.

2.2. Syntheses

2.2.1. *trans*-L_2PdCl_2, $L = Ph_2PC_5H_8CN$ (*cis or trans isomer*) *and* $Ph_2PC_6H_{10}CN$

In a typical reaction, $PdCl_2$ (0.31 g, 1.7 mmol) was dissolved in 4 ml of warm, concentrated hydrochloric acid. This solution was diluted with 50 ml of absolute ethanol and then filtered. The filtrate was added dropwise to a solution of $Ph_2PC_6H_{10}CN$ (1.02 g, 3.48 mmol) in 75 ml of absolute ethanol. The resulting mixture was stirred under ambient conditions for 4 h and then diluted with 50 ml of water. The yellow precipitate which had formed was collected on a filter and washed with ether. The yield was 1.20 g (90%).

All three products were obtained as yellow precipitates in yields that ranged from 58%–96%. No attempt was made to optimize the yields. The analytical samples of all three compounds were prepared by crystallizing the crude materials from mixtures of dichloromethane and hexane.

2.2.2. *cis*-$(Ph_2PC_6H_{10}CN)_2PtCl_2$

A solution of $Ph_2C_6H_{10}CN$ (1.05 g, 3.58 mmol) in 50 ml of 60% aqueous ethanol was added to K_2PtCl_4 (0.75 g, 1.8 mmol) dissolved in 50 ml of 40% aqueous ethanol. The mixture was stirred under ambient conditions for 2 h at which time the pink color characteristics of K_2PtCl_4 had disappeared, and a white precipitate had formed. The product was collected on a filter, washed with 2 × 20 ml of absolute ethanol and dried under vacuum. The dried product weighed 0.61 g (33%).

2.2.3. P–N chelated ($Ph_2PC_5H_8C(OCH_3) = NH$)-$PdCl_2$ (trans isomer) and ($Ph_2PC_6H_{10}C(OCH_3) = NH$)-$PdCl_2$

In a typical reaction, a solution of the major isomer of $Ph_2PC_6H_{10}CN$ (0.59 g, 2.0 mmol) in 100 ml of chloroform was added dropwise over 1 h to a rapidly stirred suspension of $PdCl_2$ (0.35 g, 2.0 mmol) in 100 ml of refluxing chloroform. The mixture was refluxed under nitrogen for an additional 60 h, and then it was filtered while hot. The resulting red-colored solution was evaporated to dryness to provide 0.77 g of solid. This solid was refluxed in 30 ml of methanol for 1 h. The resulting yellow-colored solution was filtered while hot through a bed of celite and charcoal. The resulting solution was evaporated slowly to provide 0.68 g (67%) of yellow crystals.

2.3. Separations; infrared and pK_a studies

2.3.1. Separation of trans and cis $Ph_2PC_5H_8CN$

In a well-ventilated fume hood, a 1.00 g sample of a crude reaction mixture estimated by ^{31}P NMR to be a 6:4 ratio of *trans*-to-*cis* isomers was dissolved in 5 ml of chloroform and placed on a 2.5 × 100 cm chromatography column which had been packed (40 cm height) in the standard way with 70–140 mesh silica gel in solvent mixture 1. The following quantities and mixtures of chloroform, benzene, and hexane were used in the order presented: 700 ml of 25%, 50%, 25% (mixture 1); 200 ml of 33%, 45%, 22%; 200 ml of 45%, 35%, 20%; 1000 ml of 60%, 25%, 15% (all percent by volume of chloroform, benzene, and hexane, respectively). The *trans* isomer eluted first. The chromatographed products were crystallized from n-propanol providing *ca.* 0.3 and 0.2 g of pure *trans* and *cis* isomers, respectively. A crystal of the latter isomer was selected for X-ray analysis.

2.3.2. Isolation of the major isomer of $Ph_2PC_6H_{10}CN$ by crystallization

Twenty five grams of a mixture estimated by ^{31}P NMR to be a 3:1 mixture was crystallized from 40 ml of 2-propanol providing 9.1 g of the major isomer which has a $\delta(P)$ of −10.0 ppm.

2.3.3. $Ni(CO)_3P(Ph)_2R$ IR and ^{31}C studies

These experiments were carried out as described earlier [2a,1a]. Deoxygenated methylene chloride (filtered through a column of activated alumina) and $CDCl_3$ were used for the IR and NMR measurements, respectively. The IR and NMR data from the two isomers of $Ph_2PC_5H_8CN$, the single isomer of $Ph_2PC_6H_{10}CN$, $Ph_2PCH_2CH_2CN$ and $Ph_2PCH_2CH(CH_3)CN$ are presented in Table 1.

2.3.4. Determination of the pK_a values for $P(Ph)_2R$

The titrations were carried out in nitromethane as described by Streuli [6]. A cell thermostated at 25.0° was used. A typical titration was carried out by using 10.0 ml of a phosphine solution prepared by dissolving 0.30 g of the solid in 25 ml of deoxygenated nitromethane. The data presented in Table 1 are the average of three titrations from two separate samples for the cyclopentane-based systems and two titrations from single samples for the remaining phosphines.

3. Results and discussion

3.1. Structural studies of the Ph₂PcycloalkylCN systems

The *cis* and *trans* isomers of $Ph_2PC_5H_8CN$ have been separated by column chromatography, and a sample of the isomer with the more shielded ^{31}P signal

TABLE 4. Crystal and refinement information

Formula:	$C_{18}H_{18}PN$
Crystal system:	orthorhombic
Space group:	$P2_12_12_1$
Cell dimensions (Å) at −155°C:	a = 12.404(4), b = 21.552(7), c = 5.579(1)
Vol. (Å^3):	1491.32
Calcd density (g/cm^3):	1.244
Z (molecules/cell):	4
Data collection limits; min and max 2θ (deg)	6–45
No. of reflections collected:	2266
No. of unique intensities:	1984
No. with $F_o^2 > 2.33\sigma(F_o^2)$:	1632
Final residuals; $R_{(f)}$, $R_{w(f)}$	0.0709, 0.0678

TABLE 5. Coordinates ($\times 10^4$) and isotropic thermal parameters ($\times 10$) for *cis* $Ph_2PC_5H_8CN$ [a]

Atom	*x*	*y*	*z*	B_{iso}
P(1)	4898(1)	8747(1)	6634(3)	22
C(2)	6355(4)	8924(2)	6718(11)	20
C(3)	6814(5)	9274(3)	8575(12)	25
C(4)	7910(5)	9421(3)	8516(13)	26
C(5)	8533(4)	9220(3)	6612(13)	25
C(6)	8097(5)	8869(3)	4797(12)	27
C(7)	6998(4)	8717(3)	4889(11)	25
C(8)	4364(4)	9517(3)	7421(11)	22
C(9)	4519(5)	9981(3)	5776(12)	26
C(10)	4156(5)	10 578(4)	6163(17)	36
C(11)	3609(5)	10 719(3)	8231(17)	33
C(12)	3444(5)	10 259(3)	9917(14)	29
C(13)	3828(4)	9666(3)	9558(12)	23
C(14)	4740(4)	8297(3)	9428(10)	21
C(15)	5424(6)	7696(3)	9420(16)	34
C(16)	4857(7)	7292(4)	11 349(20)	47
C(17)	3712(7)	7411(4)	11 039(18)	41
C(18)	3580(5)	8058(3)	9984(13)	27
C(19)	2885(6)	8048(4)	7945(15)	44
N(30)	2318(6)	8009(4)	6233(18)	81

[a] Estimated standard deviations are given in parentheses. Equivalent isotropic thermal parameters were estimated by using the formula presented by W.C. Hamilton, *Acta Crystallogr.*, *12* (1959) 609.

(−11.3 ppm) was crystallized from n-propanol and analyzed by X-ray methods. Crystallographic data, atomic coordinates and isotropic thermal parameters, as well as selected bond lengths and angles are summarized in Tables 4–7. An ORTEP diagram and the atom numbering scheme are presented in Fig. 1. As shown, the compound selected for study is the *cis* isomer (R, R) with the Ph_2P and CN groups in equatorial (on the "flap") and axial positions, respectively. This result confirms our prediction that the isomer with the up-

TABLE 6. Bond distances (Å) for *cis*-$Ph_2PC_5H_8CN$

P(1)–C(2)	1.847(5)
P(1)–C(8)	1.840(6)
P(1)–C(14)	1.846(6)
N(30)–C(19)	1.189(11)
C(2)–C(3)	1.402(8)
C(2)–C(7)	1.370(8)
C(3)–C(4)	1.396(8)
C(4)–C(5)	1.383(9)
C(5)–C(6)	1.375(9)
C(6)–C(7)	1.404(8)
C(8)–C(9)	1.370(8)
C(8)–C(13)	1.402(8)
C(9)–C(10)	1.381(10)
C(10)–C(11)	1.372(12)
C(11)–C(12)	1.381(10)
C(12)–C(13)	1.379(9)
C(14)–C(15)	1.549(9)
C(14)–C(18)	1.560(8)
C(15)–C(16)	1.553(11)
C(16)–C(17)	1.453(11)
C(17)–C(18)	1.523(10)
C(18)–C(19)	1.427(10)

TABLE 7. Bond angles (deg) for *cis*-$Ph_2PC_5H_8CN$

C(2)–P(1)–C(8)	99.24(24)
C(2)–P(1)–C(14)	101.02(25)
C(8)–P(1)–C(14)	103.56(27)
P(1)–C(2)–C(3)	121.8(4)
P(1)–C(2)–C(7)	118.9(5)
C(3)–C(2)–C(7)	119.3(5)
C(2)–C(3)–C(4)	120.0(6)
C(3)–C(4)–C(5)	119.4(6)
C(4)–C(5)–C(6)	121.2(5)
C(5)–C(6)–C(7)	118.9(6)
C(2)–C(7)–C(6)	121.1(6)
P(1)–C(8)–C(9)	116.6(5)
P(1)–C(8)–C(13)	125.4(5)
C(9)–C(8)–C(13)	118.0(6)
C(8)–C(9)–C(10)	121.9(7)
C(9)–C(10)–C(11)	119.9(7)
C(10)–C(11)–C(12)	119.2(7)
C(11)–C(12)–C(13)	121.0(7)
C(8)–C(13)–C(12)	119.9(6)
P(1)–C(14)–C(15)	112.3(5)
P(1)–C(14)–C(18)	116.1(4)
C(15)–C(14)–C(18)	103.3(5)
C(14)–C(15)–C(16)	102.7(6)
C(15)–C(16)–C(17)	105.1(7)
C(16)–C(17)–C(18)	108.3(6)
C(14)–C(18)–C(17)	106.3(5)
C(14)–C(18)–C(19)	113.8(6)
C(17)–C(18)–C(19)	111.1(7)
N(30)–C(19)–C(18)	176.6(10)

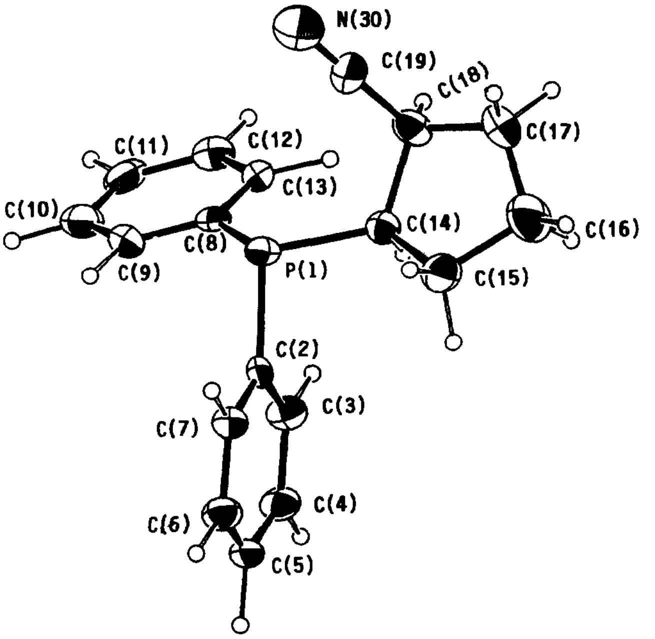

Fig. 1. ORTEP diagram of *cis*-$Ph_2PC_5H_8CN$.

field δ(C) for the CN carbon (120.9 *vs.* 122.3 ppm) would be the *cis* isomer [3]. With this X-ray result and the parallel δ(C) argument, it is also proposed that the single isomer of $Ph_2PC_6H_{10}CN$ obtained by crystallization is also the *cis* form.

In regard to the X-ray structure, bond angles and distances are in the expected ranges. The C–P–C angles of 99.20°, 101.00°, and 103.54° are similar to the 103.33°, 102.07°, and 103.57°, reported for triphenylphosphine [7]. With the exception of the C16–C17 distance, the carbon–carbon distances in the five-membered ring are *ca.* 1.55 Å which is similar to the values reported for cyclopentane [8] and *trans* 1,2-cyclopentanedicarboxylic acid [9]. Further, the angle between the planes defined by the two phenyl rings is 101.76° compared to 83.99°, 101.89°, and 103.54° for triphenylphosphine [7]. Although the five-membered ring is basically of envelope form, it is slightly puckered. The result is that C16 and C17 are 0.84 and 0.45 Å, respectively, above the plane defined C14, C15 and C18.

A prominent feature of the structure is that the CN group is directed toward the phosphorus lone pair. In order to help describe this orientation and to aid in the upcoming discussion of cone angles, a dummy atom (DU) was located 2.28 Å from the phosphorus by using the "add atom" function of the SYBYL [10] program. The DU–N and DU–C19 distances are 2.97 and 3.17 Å, respectively, and the DU–P–C19–N torsion angle is 25.5°.

Clearly, the CN group is located so that it could block the phosphorus lone pair. From another perspective, any similarly-positioned substituent could be expected to substantially affect the cone angle of a phosphine. Although, carbocycle conformational, and P–C rotational, changes could result in structures in which the substituent would be unobtrusive, these would be expected to be of higher energy and, even if the group was pointed away from the lone pair, it would be in a position to increase the C–P–C angles. These two limiting arrangements, shown schematically in Fig. 2, correspond to front and back strain.

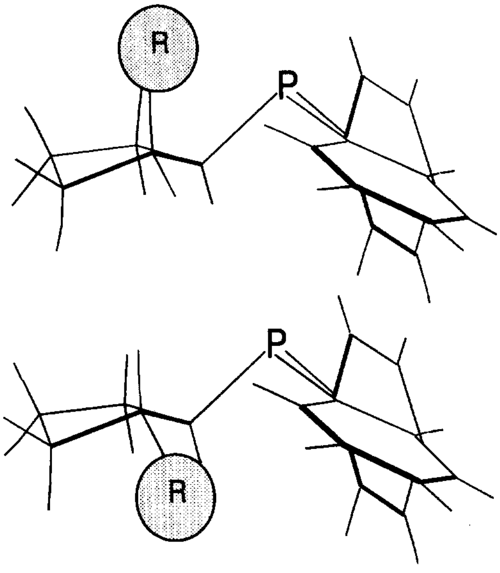

Fig. 2. "R up" and "R down" arrangements.

For the *cis* isomer, the possibilities for additional low energy conformations were examined in two ways by use of the SYBYL program. For both studies, the X-ray-determined structure was used as the input data, the P–C bonds were defined as rotatable and all C–P–C angles were constrained to the input values. In the first study, the van der Waals energies (VDW factor = 0.80) of the 21 lowest energy conformers with energies ranging from 73.6 through the minimum at 54.1 to 70.4 Kcal/mol were obtained and examined. An analysis of these conformers gives rise to two conclusions. First, compared to a relative energy of 54.3 Kcal/mol for the conformation from the X-ray results, the calculated minimum was in good agreement at 54.1 Kcal/mol. Second, in all 21 conformers, the CN group was generally in the "up" position as illustrated in Fig. 2. Further, all except one of the Du–N distances ranged from 2.45 to 3.00 Å (the distance in the X-ray structure is

TABLE 8. Selected torsion angles (deg) and calculated Tolman cone angles (θ) for *cis* and *trans* isomers of 2-diphenylphosphino-1-Rcyclopentanes

Isomer	data set [a]	R	DU–P–C14–C-18	DU–P–C2–C7	DU–P–C8–C9	plane angle	θ
cis	1	CN	−51.7	−7.7	−59.8	101.8	171
cis	2	CN	−49.5	−7.7	−59.8	101.8	172
cis	3	CN	−53.3	−9.9	−57.2	100.8	173
trans	3	CN	−51.3	−6.5	−56.9	100.5	151
cis	3	CH_3	−52.3	−7.6	−60.1	102.0	162
trans	3	CH_3	−53.0	−8.0	−29.8	80.7	158
–	3	H	−52.4	−10.5	−57.6	102.2	151

[a] Data set identification: 1) X-ray structure, 2) SYBYL VDW energy minimization 3) SYBYL molecular mechanics minimization.

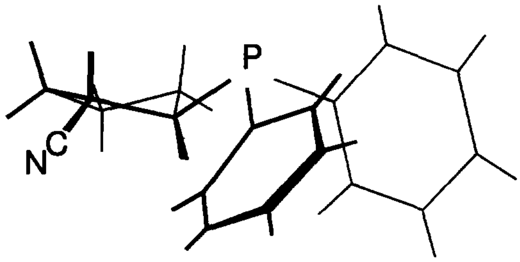

Fig. 3. Proposed structure for *trans*-$Ph_2PC_5H_8CN$.

2.98 Å) and the outlying value of 3.16 Å was associated with the highest energy conformer. In the second study, the SYBYL molecular mechanics program was used to obtain an energy minimized structure. Again, the geometry obtained (see Table 8) was similar to the X-ray-based result.

In the absence of structural data, questions remain regarding the conformations for the corresponding *trans* isomer. In order to explore possibilities, a molecular mechanics calculation has also been carried out on an input geometry generated from the *cis* isomer by moving the smaller CN group to the equatorial position. With the C–P–C angles constrained to the X-ray-determined values, the energy minimization provided the structure shown in Fig. 3. Clearly the CN group is in an arrangement which is closer to the "R down" rather than "R up" arrangement.

As reported earlier [3], the *trans* and *cis* isomers for the cyclopentane-based systems provide ^{31}P shifts of -3.8 and -11.3 ppm, respectively, values which indicate a considerable average difference for the phosphorus environments. Further, the values obtained for the analogous cyclohexane-based systems (-10.0 and -10.9 ppm) suggest that the trans isomer has the unusual chemical shift value. It has previously been reported that the *Z* and *E* isomers of $Ph_2PCH{=}CHCH_3$ provide ^{31}P shifts of -32.7 and -14.2 ppm, respectively, and an an explanation for this γ effect is that phosphines with groups which are in a position to "compress' the phosphorus lone pair have upfield chemical shifts [11a]. Since downfield ^{31}P signals are usually associated with the larger C–P–C angles [2c, 11b], it is also possible that the *trans* isomer has the CN and Ph_2P groups located on the cyclopentane ring in a fashion that tends to increase the C–P–C angles.

As indicated above, it is recognized that the cyano group is a good ligand in its own right [4], and this coupled with the fact that it is sterically undemanding make it challenging to define the cone angles for these ligands. However, the question of how sterically hindered this type of phosphorus might be has been evaluated by using Tolman's definition of cone angles generated from three $\theta/2$ values [2c]. For these analyses, hydrogen and nitrogen van der Waals radii were set at 1.2 Å and 1.5 Å, respectively, and the C–H distances were set at 1.1 Å.

The results for the *cis* and *trans* isomers of the cyano derivatives as well as the energy minimized CH_3 and unsubstituted analogues are presented in Table 8. It should be noted that the input geometries for both the CH_3- and H-substituted analogues were obtained from the X-ray-generated results as described above for the cyano compounds. Two observations arise from these results. First, the *cis* isomers are slightly larger than the *trans* isomers, and the effect of adding a methyl substituent in the number two position increases the cone angle of the ligand by about 10°. In regard to the latter point, MINDO/3-data-generated cone angles [12] for H_2PPh and $H_2P(o\text{-}PhCH_3)$ were calculated to be 104° and 111°, respectively, a difference which is comparable to what was obtained from this study.

Given the methods used, the cone angles determined for these ligands, especially for *cis* $Ph_2PC_5H_8$-CN, are likely too high. The value for $Ph_2PC_5H_9$, 151°, however, is close to the value of 153 determined for $Ph_2PC_6H_{11}$ [2c].

3.2. pK_a *measurements and IR and NMR studies on Ni complexes*

In order to further assess the donor/acceptor abilities of these phosphines, pK_a measurements on the free phosphines and spectroscopic (^{13}C and IR) measurements on $Ni(CO)_3L$ complexes have been carried out. As summarized in Table 1, these measurements are consistent with the conclusion that all three of the cyanocycloalkyl derivatives have similar basicities and donor/acceptor properties. Further, all the cyano phosphines listed are weaker bases than PPh_3, $pK_a = 2.73$, but, the acyclic $Ph_2PCH_2CH_2CN$ is the weakest base in the set. It is proposed, however, that, compared to the *cis* isomer, the *trans* $Ph_2PC_5H_8CN$ is slightly more basic. Although the results are similar, the pK_a measurements carried out on multiple samples on three different days all consistently identified the *trans* isomer as the stronger base by *ca.* 0.10 pK_a unit.

As summarized in Table 1, NMR and IR data for the $Ni(CO)_3L$ complexes of these ligands have also been obtained. The donor/acceptor ratio as evinced by the ^{13}C chemical shifts are similar for all three of the cycloalkyl-based systems and greater than that observed for the acyclic systems. Clearly these Ni-based data indicate that these ligands are similar in effect to $Ph_2P(OR)$ and $PhP(OR)_2$. For example, the reported ^{13}C chemical shift (downfield from $Ni(CO)_4$) for $PhP(OBu)_2$ is 4.20 ppm [1a].

Giering has recently presented evidence which supports the idea that $Ph_2PCH_2CH_2CN$ can be classified as a group 1 or σ-donor only ligand. Further, he has shown that for such ligands the following relationship holds [1f].

$$pK_a = -0.68(+/-0.03)X\text{-}0.047(+/-0.010)\theta$$
$$+18.9(+/-1.6)$$

X = difference between A_1 band for $Ni(CO)_3L$ and 2056.1 cm^{-1}

θ = *cone angle*

Using this relationship along with the pK_a values and the $Ni(CO)_3L$ $\nu(CO)$ values that we have determined leads to calculated (−0.68) and −0.047) cone angles of 136°, 142°, 146°, and 128° and 125° for *cis* and *trans* $Ph_2PC_5H_8CN$, $Ph_2PC_6H_{10}CN$, $Ph_2PCH_2CH(CH_3)CN$ and $Ph_2PCH_2CH_2CN$, respectively, values which are lower than expected on the basis of cone angles reported for similar ligands [2c,1f]. Treating these four ligands as a set and assumming that $Ph_2PCH_2CH_2CN$ has a cone angle of about 142° [1f], adjusting the coefficient from 18.9 to 19.7 gives cone angles of 159°, 164°, 163°, 145° and 142°, respectively, values which are more in line with those reported and our calculated values.

The ^{13}C spectra (aliphatic and aromatic regions) of the $Ni(CO)_3L$ complexes are consistent with the formation of phosphine complexes with the nitrile groups being uncoordinated. As will also be evident from the data presented below for the platinum and palladium complexes, support for this conclusion arises from the $J(PC)$ values for the *ipso* carbons of the phenyl rings and the sp^3 carbons (C_1 carbons) attached to the phosphorus atoms as well as the chemical shifts of the CN carbons. In regard to the latter, compared to the free ligands, the CN carbon signals observed for the nickel complexes are all *ca.* 0.5 ppm upfield whereas a downfield shift is expected if the CN group coordinates [5,13]. Further, as expected [14], the $J(PC)$ for the *ipso* carbons all increase from *ca.* 12–15 to 30–33 Hz, and the values for the C_1 carbons increase from 3.7–8.0 Hz. For example, the spectra (chemical shifts in ppm and $J(PC)$ in Hz) from the free ligand and complex containing *cis*-$Ph_2PC_5H_8CN$ contain two doublets for the diastereotopic *ipso* carbons at 137.1 ($J = 14.0$), 136.5 ($J = 12.4$) for the free ligand and 136.9 ($J = 32.6$) and 134.7 ($J = 31.3$) for the complex. Similarly, for the C_1 carbons the values are 40.5 ($J = 12.5$) and 40.7 ($J = 16.9$), respectively.

In order to further evaluate the ligand properties of these mixed donor ligands, platinum(II) and palladium(II) complexes (see Tables 2 and 3) have been prepared. As expected, all three of the cycloalkane-based ligands readily form stable complexes of stoichiometry L_2PdCl_2. The IR and NMR data are all consistent with the formulation of these as *trans*-substituted phosphine complexes. Clearly, the $\nu(CN)$ bands are observed near the frequencies measured for the free ligands, a situation which is consistent with free nitrile groups [4]. Further the $\nu(PdCl)$ and ^{31}P data are entirely consistent with *trans*, rather than *cis*, complexes [5,14]. As observed for the *ipso* carbon for the $Ni(CO)_3L$ complexes, the diastereotopic phosphorus atoms in these complexes are distinguishable and are separated by *ca.* 0.10 ppm; a difference of this magnitude was previously reported for the diastereotopic phosphorus atoms in $PdCl_2(Ph_2PCH_2CH(CH_3)CN)_2$ [5].

The platinum complex is assigned a *trans* geometry on the basis of the $J(PtP)$ value of 2,524 Hz [14]. In contrast to the Pd complexes, the diastereotopic phosphorus atoms could not be distinguished even though the ^{31}P experiment had been carried out several times on three different instruments. In comparison with previously reported results, it is noted that the $PtCl_2(Ph_{3-x}P(CH_2CH_2CN)_x$ are *cis* with the exception of the case with $X = 3$ for which both isomers are observed [13].

The nitrile groups in the acyclic ($Ph_2PCH_2CH(R)CN$; R = H, CH_3) and aromatic (Ph_2P-*o*-C_6H_4CN) analogues of these readily react with alcohols to form imidates or imino ethers when coordinated to palladium to 1:1, $LPdX_2$, fashion [5]. Both *trans* $Ph_2PC_5H_8CN$ and $Ph_2PC_6H_{10}CN$ undergo similar reactions, and the resulting complexes provide analytical and spectroscopic data which are completely consistent with the formation of P–N chelates of the type shown in Fig. 4.

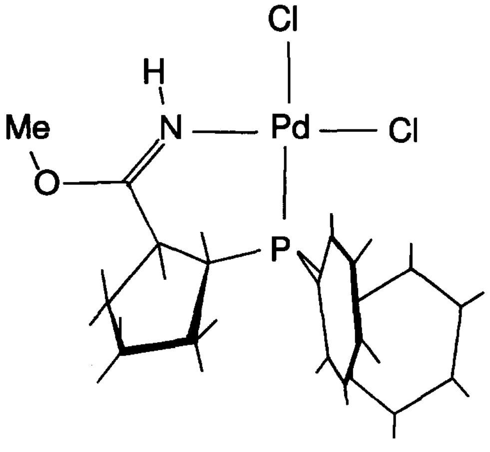

Fig. 4. Proposed structure for imino ether complexes.

Acknowledgments

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society and the Ball State University Faculty Grants Program for support of this Research. Special thanks to John C. Huffman, Indiana University Molecular Structure Center for his assistance and encouragement.

References

1 (a) G.M. Bodner, M.P. May and L.E. McKinney, *Inorg. Chem., 19* (1980) 1951; (b) T. Bartik, T. Himmler, H.G. Schulte and K. Seevogel, *J. Organomet. Chem., 272* (1984) 29; (c) T. Bartik and T. Himmler, *J. Organomet. Chem., 293* (1985) 343; (d) G.M. Bancroft, L. Dignard-Bailey and R.J. Puddephatt, *Inorg. Chem., 25* (1986) 3675; (e) Md. M. Rahman, H.-Y. Liu, K. Eriks, A. Prock and W.P. Giering, *Organometallics, 8* (1989) 1; (f) H.-Y. Liu, K. Eriks, A. Prock and W.P. Giering, *Organometallics, 9* (1990) 1758; (g) J.S. Panek, A. Prock, K. Eriks and W.P. Giering, *Organometallics, 9* (1990) 2175; (h) A.G. Orpen and N.G. Connelly, *Organometallics, 9* (1990) 1206; (i) A. Miedaner, R.C. Haltiwanger and D.L. DuBois, *Inorg. Chem., 30* (1991) 417; (j) J.R. Sowa, Jr. and R.J. Angelici, *Inorg. Chem., 30* (1991) 3534; (k) R. Romeo, G. Arena and L.M. Scolaro, *Inorg. Chem., 31* (1992) 4879; (l) J. Polowin, S.C. Mackie and M.C. Baird, *Organometallics, 11* (1992) 3724; (m) D.C. Woska, M. Wilson, J. Bartholomew, K. Eriks, A. Prock and W.P. Giering, *Organometallics, 11* (1992) 3343; (n) T.L. Brown, *Inorg. Chem., 31* (1992) 1286; (o) D.C. Woska, J. Bartholomew, J.E. Greene, K. Eriks, A. Prock and W.P. Giering, *Organometallics, 12*, (1993) 304.

2 (a) C.A. Tolman, *J. Am. Chem. Soc., 92* (1970) 2953; (b) C.A. Tolman, *J. Am. Chem. Soc., 92* (1970) 2956; (c) C.A. Tolman, *Chem. Rev., 77* (1977) 313.

3 D.A. Blinn, R.S. Button, V. Farazi, M.K. Neeb, C.L. Tapley, T.E. Trehearne, S.D. West, T.L. Kruger and B.N. Storhoff, *J. Organomet. Chem., 393* (1990) 143.

4 (a) B.N. Storhoff and H.C. Lewis, Jr., *Coord. Chem. Rev., 23* (1977) 1; (b) V.W. Wolfsberger, *Chemiker-Zeit., 114* (1990) 275.

5 M. Habib, H. Trujillo, C.A. Alexander and B.N. Storhoff, *Inorg. Chem., 24* (1985) 2344.

6 (a) C.A. Streuli, *Anal. Chem., 31* (1959) 1652; (b) C.A. Streuli, *Anal. Chem., 32* (1960) 985.

7 J.J. Daly, *J. Chem. Soc.*, (1964) 3799.

8 W.J. Adams, H.J. Geise and L.S. Bartell, *J. Am. Chem. Soc., 92* (1970) 5013.

9 E. Benedetti, P. Corradini and C. Pedone, *J. Phys. Chem., 76* (1972) 790.

10 The SYBYL program set was obtained from TRIPOS Associates, Inc., St. Louis, MO, USA.

11 (a) S.O. Grim, R.P. Molenda and J.D. Mitchell, *J. Org. Chem., 45* (1980) 250; (b) S.O. Grim, W. McFarlane and E.F. Davidoff, *J. Org. Chem., 32* (1967) 781.

12 J.T. Desanto, J.A. Mosbo, B.N. Storhoff, P.L. Bock and R.E. Bloss, *Inorg. Chem., 19* (1980) 3086.

13 M.S. Holt and J.H. Nelson, *Inorg. Chem., 25* (1986) 1316.

14 P.S. Pregosin and R.W. Kunz, *^{31}P and ^{13}C NMR of Transition Metal Phosphine Complexes*, Springer-Verlag, New York, 1979.