(maximum shift/error 0.20) to the agreement indices $R = 0.0401$ ($R_w = 0.0586$) for 6739 reflections with $I > 3\sigma(I)$. Weights in the final cycle were given by $w = 4F^2[\sigma(I)^2 + (0.035F^2)^2]^{-1}$, the esd of an observation of unit weight was 2.16, and a final difference Fourier was featureless. A PDP 11/23 computer and programs in the Enraf-Nonius SDP package[29] were used for the refinement.

Acknowledgment. This work was supported by grants from the Natural Sciences and Engineering Research Council of Canada who also awarded T.G.S. a scholarship.

Registry No. **1**, 96532-16-0; **2**·BF_4, 96532-18-2; **4**·BF_4, 96532-20-6; **7**, 96532-21-7; **8**, 96532-22-8; **9**, 96532-23-9; **10**, 96532-24-0; **11**, 96532-26-2; **12**, 96532-27-3; **13**, 96532-28-4; **14**, 96532-29-5; **15**, 96532-30-8; **16**, 96532-31-9; CH_3COCl, 75-36-5; CH_3I, 74-88-4; $Ir_2H_2(COD)_2PNNP^+$, 96555-14-5; $PhCH{=}CH_2$, 100-42-5; $PhC{\equiv}CPh$, 588-59-0; $CH_2{=}C(CH_3)CH{=}CH_2$, 78-79-5; $CH_2{=}CHCOH$, 107-02-8; $CH_2{=}CHCH_2CH_2CH{=}CH_2$, 592-42-7; $PhCH_2CH_3$, 100-41-4; *cis*-$PhCH{=}CHPh$, 645-49-8; *trans*-$PhCH{=}CHPh$, 103-30-0; $PhCH_2CH_2Ph$, 103-29-7; 1,3-cyclohexadiene, 592-57-4; 1,3-cyclooctadiene, 1700-10-3; benzene, 71-43-2; cyclohexane, 110-82-7.

Supplementary Material Available: Tables of hydrogen atom positions, general temperature factor expressions, bond distances and bond angles, and final structure factor amplitudes for **11** (45 pages). Ordering information is given on any current masthead page.

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Syntheses, Characterization, and Properties of Palladium(II) Complexes Containing Bidentate Phosphine–Nitrile or Phosphine–Imidate Ligands

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Received September 14, 1984

The reactions of H_2PdX_4 (X = Cl, Br) with $Ph_2PCH_2CH(CH_3)CN$, $Ph_2P(CH_2)_2CN$, or $Ph_2P(o\text{-}C_6H_4CN)$ (L) in a 1.0:2.1 mole ratio yield the corresponding *trans*-PdX_2L_2 complexes in which the L groups function as monodentate phosphines. For the case in which L = $Ph_2PCH_2CH(CH_3)CN$, both ^{31}P and ^{13}C NMR measurements indicate the presence of approximately equal quantities of each diastereomer. For the latter two ligands, complexes of stoichiometry $[LPdX_2]_2$ are also readily obtained. For the $Ph_2P(o\text{-}C_6H_4CN)$-based dimers, IR and NMR data are consistent with halogen-bridged formulations. Similary obtained data from the $Ph_2P(CH_2)_2CN$-containing dimers indicate the presence of more than one isomer. These data are rationalized on the basis of halogen-bridged and ligand-bridged dimers that interconvert rapidly on the NMR time scale. The nitrile groups in all the dimeric complexes react with alcohols (methanol and/or ethanol) to yield the corresponding chelated phosphine–imidate complexes.

Introduction

Bidentate ligands with two types of donor sites are well-known and have been the subject of many reports. Ligands of this general type are of interest because they can bridge dissimilar metals or, if one donor is easily replaced, yield complexes that readily provide a coordination site for incoming substrates.[1,2] Included, for example, are phosphines that also contain a carbon,[3] nitrogen,[4–11] oxygen,[12–15] or sulfur[16–18] donor atom. Of the nitrogen-containing phosphines, 2-(diphenylphosphino)pyridine,[4] 3-(diphenylphosphino)-*N*,*N*-dimethylpropylamine,[6,7] 3-(diphenylphosphino)propionitrile,[10] and *o*-(diphenylphosphino)benzonitrile[11] are four examples that collectively function as both chelating and bridging ligands. The ligand properties of 2-(diphenylphosphino)pyridine are, in particular, well established and provide homonuclear and heteronuclear ligand-bridged dimers of diverse reactivities.[4,19–22]

We have reported rhenium(I) complexes of the stoichiometry $Re_2(CO)_6L_2X_2$ (L = 3-(diphenylphosphino)propionitrile, *o*-(diphenylphosphino)benzonitrile; X = Cl, Br).[10,11] From spectroscopic data, we concluded that these complexes were ligand- rather than halogen-bridged dimers in which the nitrile groups coordinated in end-on fashion. As expected,[2] the nitrile groups in these complexes could be readily replaced by a variety of other donors. To further establish the nature of phosphine–nitrile ligands, we have now synthesized several palladium(II) complexes of 3-(di-

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phenylphosphino)propionitrile (DPPN) and *o*-(diphenylphosphino)benzonitrile (DPBN) as well as 3-(diphenylphosphino)-2-methylpropionitrile ($Ph_2PCH_2CH(CH_3)CN$; DPMN). Herein we summarize the results from that study.

Experimental Section

General Information. Palladium chloride (Fisher Scientific Co.), diphenylphosphine (Strem Chemicals, Inc.), acrylonitrile (Aldrich Chemical Co.), and methacrylonitrile (Aldrich Chemical Co.) were purchased from the sources indicated. *o*-(Diphenylphosphino)benzonitrile[23] and Na_2PdX_4[24] (X = Cl, Br) were prepared by literature methods. All solvents, including methanol and absolute ethanol, were reagent grade and were used as received. All reactions were carried out under a nitrogen atmosphere.

Infrared spectra (4000–200 cm^{-1}) were recorded on either a Beckman 4250 spectrophotometer that was calibrated with polystyrene or an Analect FX 6200 instrument. Ultraviolet–visible spectra (250–600 nm) were recorded on a Beckman DK-2A instrument. With the exceptions noted below, the ambient-temperature nuclear magnetic resonance spectra (^{13}C, ^{31}P) were recorded on a Varian FT-80A spectrometer. The variable-temperature ^{31}P NMR studies were carried out on a Bruker HX90E. The ^1H, ^{13}C, and ^{31}P NMR spectra of $PdCl_2[Ph_2PCH_2CH(CH_3)CN]_2$ were also recorded with an NT-200 instrument. To reduce data acquisition time, $Cr(acac)_3$ (acac = acetylacetonate) was added to the samples prior to collecting ^{13}C NMR data. Molecular weights were determined by using a Hitachi Perkin-Elmer Model 115 molecular weight apparatus. Melting points were measured on an electrothermal melting point apparatus and are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN, or Midwest Microlab, Ltd., Indianapolis, IN.

Syntheses. 3-(Diphenylphosphino)propionitrile ($Ph_2P(CH_2)_2CN$[25]). Freshly distilled acrylonitrile (12.0 g, 0.226 mol) was added over a 0.5-h period to a stirred mixture of diphenylphosphine (25.0 g, 0.134 mol), 50 mL of acetonitrile, and 1 mL of 50% aqueous sodium hydroxide that was maintained below 25 °C. After the addition, the reaction mixture was warmed to 55 °C and stirred for an additional 1 h. The organic layer was separated, washed with three 10-mL portions of saturated aqueous sodium chloride, dried with anhydrous sodium sulfate, and distilled. The fraction boiling from 180 to 190 °C at 0.2 torr was collected (28.6 g, 89%). The resulting coloreless oil slowly crystallized.

3-(Diphenylphosphino)2-methylpropionitrile ($Ph_2PCH_2CH(CH_3)CN$). Freshly distilled methacrylonitrile (16.0 g, 0.238 mol) was added dropwise over 1 h to a stirred mixture of diphenylphosphine (21.5 g, 0.115 mol), 50 mL of acetonitrile, and 0.5 mL of 50% aqueous sodium hydroxide that was maintained at 50 °C. After the addition, the mixture was stirred for an additional 0.5 h at 50 °C. Dichloromethane and water, 25 mL of each, were added to the mixture. The water layer was separated and washed with two more 25-mL portions of dichloromethane. The dichloromethane extracts were combined and dried over magnesium sulfate. The solvents were removed with a rotary evaporator, providing a colorless oil that solidified upon standing overnight. The resulting solid was recrystallized from ethanol, yielding 25.3 g (87%) of colorless crystals.

$PdCl_2L_2$ (L = $Ph_2P(CH_2)_2CN$, $Ph_2PCH_2CH(CH_3)CN$, $Ph_2P(o\text{-}C_6H_4CN)$). In a representative reaction, palladium(II) chloride (0.44 g, 2.5 mmol) was dissolved in 6 mL of warm, concentrated hydrochloric acid. The resulting solution was diluted with 50 mL of absolute alcohol and filtered. Under ambient conditions, the filtrate was added to a stirred solution of $Ph_2P(CH_2)_2CN$ (1.23 g, 5.14 mmol) in 70 mL of absolute ethanol. A yellow precipitate formed immediately, but the mixture was stirred for an additional 4 h. The precipitate was collected on a filter and washed twice with 15 mL of water and twice with 15 mL of ether. The product weighed 1.57 g (96%).

All products were obtained as yellow precipitates with yields that ranged from 68–96%. No attempt was made to maximize yields. The products could be crystallized from mixtures of dichloromethane or chloroform and hexane or ethanol.

$PdBr_2L_2$ (L = $Ph_2P(CH_2)_2CN$, $Ph_2PCH_2CH(CH_3)CN$). Both complexes were prepared from LiBr and $PdCl_2L_2$ in acetone. For example, LiBr (0.27, 3.1 mmol), $PdCl_2[Ph_2P(CH_2)_2CN]_2$ (0.20 g, 0.31 mmol), and 25 mL of acetone were stirred at ambient conditions for 3 h. The resulting solution was evaporated to dryness and the residue washed with three 10-mL portions each of water and ethanol. The resulting solid was recrystallized from dichloromethane–hexane, providing 0.18 g (88%) of product.

$PdBr_2[Ph_2P(o\text{-}C_6H_4CN)]_2$. Palladium(II) bromide (0.20 g, 0.75 mmol) was dissolved in 4 mL of warm, 40% aqueous hydrobromic acid. The resulting solution was diluted with 40 mL of absolute ethanol and filtered. Under ambient conditions, the filtrate was added to a stirred solution of $Ph_2P(o\text{-}C_6H_4CN)$ (0.46 g, 1.6 mmol) in 15 mL of chloroform and 15 mL of ethanol. The mixture was stirred at ambient temperature for 1 h. The resulting precipitate was collected on a filter and washed with two 20-mL portions each of water and ethanol. The product was recrystallized from a mixture of chloroform and ethanol providing 0.42 g (60%) of product.

$[PdCl_2[Ph_2P(CH_2)_2CN]]_2$. Sodium tetrachloropalladate (0.650 g, 2.21 mmol) and $Ph_2P(CH_2)_2CN$ (0.457 g, 1.91 mmol) were refluxed in 100 mL of $CHCl_3$ for 72 h. The resulting mixture was then filtered and the orange filtrate evaporated to dryness by using a rotary evaporator. The solid was placed on a filter, washed with 20 mL of water and 20 mL of diethyl ether, and then dissolved in 25 mL of dichloromethane. This solution was treated with activated charcoal and filtered through diatomaceous earth. Hexane (25 mL) was added to the filtrate and the mixture allowed to evaporate slowly under ambient conditions until the total volume was ca. 5 mL. The precipitate present was collected on a filter, washed with 10 mL of hexane, and then dried under vacuum to yield 0.587 g (75%) of product. The electronic spectrum displayed bands at 305 and 380 nm with ϵ values (M^{-1} cm^{-1}) for 8.3×10^4 and 2.2×10^3, respectively.

$[PdBr_2[Ph_2P(CH_2)_2CN]]_2$. Palladium(II) bromide (0.745 g, 2.80 mmol), $Ph_2P(CH_2)_2CN$ (0.600 g, 2.51 mmol), and 55 mL of $CHCl_3$ were refluxed for 72 h. The reaction mixture was then filtered and 150 mL of 2-propanol added to the filtrate. The filtrate was allowed to evaporate slowly under ambient conditions until the total volume was ca. 10 mL. The resulting red-orange product was then collected on a filter and dried under vacuum. The yield was 1.10 g (87%). The electronic spectrum displayed a band at 310 nm with an ϵ value (M^{-1} cm^{-1}) of 7.7×10^3.

$[PdCl_2[Ph_2P(o\text{-}C_6H_4CN)]]_2$. A mixture of palladium(II) chloride (0.14 g, 0.79 mmol), $Ph_2P(o\text{-}C_6H_4CN)$ (0.20 g, 0.70 mmol), and 35 mL of chloroform was refluxed for 72 h. The resulting mixture was cooled to room temperature and filtered. The precipitate was refluxed for 1 h in 500 mL of chloroform and the resulting mixture filtered while hot. The filtrate was evaporated to dryness by using a rotary evaporator. The orange solid was washed with 25 mL of dichloromethane and then dried under vacuum, providing 0.29 g (91%) of product.

$[PdBr_2[Ph_2P(o\text{-}C_6H_4CN)]]_2$. Sodium tetrabromopalladate (0.44 g, 0.94 mmol), $PdBr_2[Ph_2P(o\text{-}C_6H_4CN)]_2$ (0.70 g, 0.83 mmol), and 225 mL of chloroform were refluxed for 72 h. The mixture was evaporated to dryness and washed with 25 mL of water, 25 mL of ether, and then 25 mL of dichloromethane. The precipitate was refluxed for 1 h with 500 mL of dichloromethane and then filtered. Removal of the dichloromethane by rotary evaporation provided 0.88 g (93%) of the orange product.

$PdX_2[Ph_2P(CH_2)_2C(OR)NH]$ (R = CH_3, X = Cl, Br; R = C_2H_5, X = Cl). In a typical reaction, $[PdCl_2[Ph_2P(CH_2)_2CN]]_2$ (0.42 g, 0.50 mmol) and 50 mL of methanol were refluxed for 4 h. During the reaction period, the color of the solution changed from orange to yellow. Following the reaction, methanol was removed with a rotary evaporator and the remaining solid crystallized from dichloromethane and hexane. The yield was 0.40 g (89%).

$PdCl_2[Ph_2P(o\text{-}C_6H_4C(OCH_3)NH)]$. Methanol (30 mL) and $[PdCl_2[Ph_2P(o\text{-}C_6H_4CN)]]_2$ (0.14 g, 0.15 mmol) were refluxed for 7 h. The resulting yellow-orange solution was filtered through Celite and the filtrate allowed to evaporate slowly under ambient conditions. As the solution evaporated, yellow crystals formed, which were collected on a filter. The product weighed 0.11 g (73%).

$PdCl_2[Ph_2P(o\text{-}C_6H_4C(OC_2H_5)NH)]$. Palladium(II) chloride (0.044 g, 0.25 mmol) was dissolved in 3 mL of warm, concentrated hydrochloric acid. The resulting solution was diluted with 25 mL of 95% aqueous ethanol. To this solution was added $PdCl_2[Ph_2P(o\text{-}C_6H_4CN)]_2$ (0.17 g, 0.23 mmol), and the mixture was refluxed for 8 h. Following the reaction period, the solution was filtered and the filtrate evaporated to dryness. The solid was washed with two 10-mL portions each of water and 95% ethanol. The yellow solid was dried under vacuum for 24 h, yielding 0.15 g (70%) of product.

Results and Discussion

Complexes of Stoichiometry PdX_2L_2. The reaction of H_2PdX_4 with 2.1 molar equiv of DPPN (X = Cl), DPMN (X = Cl), or DPBN (X = Cl, Br) in ethanol yields yellow precipitates of stoichiometry PdX_2L_2. For convenience, metathesis reactions using LiBr were used to obtain the analogous $PdBr_2(DPPN)_2$ and

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Table I. Analytical and Melting Point Data

compd	mp,[a] °C	% C calcd	% C found	% H calcd	% H found	% N calcd	% N found	mol wt[b] calcd	mol wt[b] found
$Ph_2PCH_2CH(CH_3)CN$	44–45	75.87	76.05	6.37	6.18	5.53	5.40		
$PdCl_2[Ph_2P(CH_2)_2CN]_2$	210–212	54.94	55.03	4.30	4.40	4.27	4.14	656	695
$PdBr_2[Ph_2P(CH_2)_2CN]_2$	200–202	48.38	48.50	3.79	3.84	3.76	3.60	745	732
$PdCl_2[Ph_2PCH_2CH(CH_3)CN]_2$	169–170	56.20	56.11	4.72	4.87	4.10	3.96	684	709
$PdBr_2[Ph_2PCH_2CH(CH_3)CN]_2{}^c$	192–197	49.74	49.59	4.17	4.28	3.62	3.62		
$PdCl_2[Ph_2P(o\text{-}C_6H_4CN)]_2\cdot{}^1/_4CH_2Cl_2$	264–268	59.42	59.04	3.72	3.42	3.62	3.62		
$PdBr_2[Ph_2P(o\text{-}C_6H_4CN)]_2$	255–258	54.28	53.44	3.36	3.08	3.33	3.49	841	804
$[PdCl_2[Ph_2P(CH_2)_2CN]]_2\cdot{}^1/_4CH_2Cl_2{}^d$	178–182	42.53	42.65	3.36	3.26	3.28	3.19	833	817
$[PdBr_2[Ph_2P(CH_2)_2CN]]_2$	190–192	35.64	36.00	2.79	2.86	2.77	2.63	1011	1006
$[PdCl_2[Ph_2P(o\text{-}C_6H_4CN)]]_2$	232–234	49.11	48.70	3.04	3.07	3.01	3.12		
$[PdBr_2[Ph_2P(o\text{-}C_6H_4CN)]]_2\cdot{}^1/_4CH_2Cl_2$	285–286	40.72	40.77	2.55	3.06	2.48	2.06	1107	1080
$PdCl_2[Ph_2P(CH_2)_2C(OCH_3)NH]$	218–220	42.84	42.72	4.04	4.01	3.12	3.22	449	450
$PdBr_2[Ph_2P(CH_2)_2C(OCH_3)NH]$	205–208	35.75	35.79	3.37	3.25	2.61	2.51	538	538
$PdCl_2[Ph_2P(CH_2)_2C(OC_2H_5)NH]$	229–230	44.13	44.21	4.36	4.41	3.03	2.98	463	497
$PdCl_2[Ph_2P(o\text{-}C_6H_4C(OCH_3)NH)]$	197–199	48.37	48.50	3.65	3.70	2.82	3.06	497	465

[a] Uncorrected. [b] Measured in $CHCl_3$ solution. [c] Percent bromine: calcd, 20.68; found, 20.88. [d] Percent chlorine: calcd, 18.67; found, 18.06.

Table II. Infrared Spectral Data[a]

compd	$\nu(PdX)^b$	$\nu(CN)$
$Ph_2P(CH_2)_2CN$		2255 (m), 2235 (sh)[c]
$Ph_2PCH_2CH(CH_3)CN$		2245 (m)[c]
$Ph_2P(o\text{-}C_6H_4CN)$		2220 (m)[c]
$PdCl_2[Ph_2P(CH_2)_2CN]_2$	340	2260, 2240[c]
$PdBr_2[Ph_2P(CH_2)_2CN]_2$	285	2260, 2240[c]
$PdCl_2[Ph_2PCH_2CH(CH_3)CN]_2$	355	2245[d]
$PdBr_2[Ph_2PCH_2CH(CH_3)CN]_2$	280	2245[d]
$PdCl_2[Ph_2P(o\text{-}C_6H_4CN)]_2\cdot{}^1/_4CH_2Cl_2$	355	2225[d]
$PdBr_2[Ph_2P(o\text{-}C_6H_4CN)]_2$	275	2225[d]
$[PdCl_2[Ph_2P(CH_2)_2CN]]_2\cdot{}^1/_4CH_2Cl_2$	350 (s), 345 (sh), 295 (w), 270 (sh), 260 (m)	2305 (w),[c] 2260 (m), 2240 (m)[b]
$[PdBr_2[Ph_2P(CH_2)_2CN]]_2$	280	2305 (vw),[c] 2260 (m), 2240 (m)
$[PdCl_2[Ph_2P(o\text{-}C_6H_4CN)]]_2$	355 (s), 295 (w), 265 (m)	2225[d]
$[PdBr_2[Ph_2P(o\text{-}C_6H_4CN)]]_2\cdot{}^1/_4CH_2Cl_2$	275	2220[d]
$PdCl_2[Ph_2P(CH_2)_2C(OCH_3)NH]$	345 (m), 285 (m)	1635[b]
$PdBr_2[Ph_2P(CH_2)_2C(OCH_3)NH]$	240	1635[b]
$PdCl_2[Ph_2P(CH_2)_2C(OC_2H_5)NH]$	355 (m), 285 (m), 280 (sh)	1635[b]
$PdCl_2[Ph_2P(o\text{-}C_6H_4C(OCH_3)NH)]$	350 (m), 275 (m)	1640[b]

[a] In cm^{-1}; sh = shoulder, br = broad. [b] Nujol mulls on polyethylene plates. [c] $CHCl_3$ solution. [d] Nujol mulls on NaCl plates.

$PdBr_2(DPMN)_2$ complexes (see Table I for the analytical data). All of these palladium complexes are stable in air, are soluble in chlorinated hydrocarbons, and form crystals readily. The DPPN- and DPMN-containing complexes are also soluble in benzene.

The IR and NMR data (see Tables II–IV) support the conclusion that the complexes are typical trans-coordinated phosphine complexes. In accord, single $\nu(MX)$ bands near 350 and 270 cm^{-1} are observed for the chloride- and bromide-containing complexes, respectively.[26,27] As expected, the $\nu(CN)$ bands are observed at or near the positions observed for the free ligands, which is consistent with uncomplexed nitrile groups.[2] Further, the proton-decoupled ^{31}P NMR spectra of $PdX_2(DPPN)$ and $PdX_2(DPBN)$ (X = Cl, Br) all display only one signal, which is consistent with the presence of single isomers. For these, the chemical shifts are clearly in the range expected for trans-coordinated phosphines.[28] For $PdCl_2(DPMN)_2$, however, two ^{31}P signals of nearly equal area are obtained with chemical shift values of 15.0 and 15.1 ppm (see Figure 1). Again, both signals are in the range expected for trans rather than cis complexes. In contrast, however, only one ^{31}P NMR signal is observed for the corresponding $PdBr_2(DPMN)_2$ complex when spectra are recorded in either $CDCl_3$ or a mixture of C_6D_6 and C_6H_6. Since the alkyl chain of DPMN contains a chiral carbon, diastereomers (*R,R*, *S,S*, and *R,S*) are expected for these complexes. Clearly, the ^{31}P NMR spectrum of the chloride-containing complex is in accord with the presence of two similar isomers, and as discussed below, the ^{13}C NMR spectra of both the chloride- and bromide-containing complexes support the conclusion that the two signals observed for $PdCl_2(DPMN)_2$ arise from diastereomers.

Table III. Phosphorus-31 Nuclear Magnetic Resonance Spectral Data[a]

compd	$\delta(P)$	$\Delta\delta(P)$
$Ph_2P(CH_2)_2CN$ (DPPN)[b]	−16.3	
$Ph_2PCH_2CH(CH_3)CN$ (DPMN)[b]	−21.0	
$Ph_2P(o\text{-}C_6H_4CN)$ (DPBN)[c]	−8.3	
$PdCl_2(DPPN)_2{}^c$	15.6	31.9
$PdBr_2(DPPN)_2{}^{c,d}$	13.5	29.8
$PdCl_2(DPMN)_2{}^c$	15.1	36.1
	15.0	36.0
$PdBr_2(DPMN)_2{}^{c,e}$	11.3	32.3
$PdCl_2(DPBN)_2{}^b$	22.7	30.3
$PdBr_2(DPBN)_2{}^c$	21.3	29.6
$Pd_2Cl_4(DPPN)_2{}^c$	29.0	45.3
$Pd_2Br_4(DPPN)_2{}^c$	30.7	47.0
$PdBr_2(DPPN\cdot MeOH)^{c,f}$	25.2	

[a] Positive values are downfield from H_3PO_4, the reference. [b] Recorded in a mixture of CD_2Cl_2 and CH_2Cl_2. [c] Recorded in $CDCl_3$. [d] A single resonance at δ 13.5 was also observed at 223 K. [e] A single resonance at δ 11.8 was also observed when the spectrum was recorded in C_6D_6. [f] DPPN·MeOH ; $Ph_2P(CH_2)_2C(OCH_3)NH$.

Carbon-13 NMR spectra ($^{13}C\{^1H\}$) have been recorded for the soluble PdX_2L_2 (X = Cl, Br; L = DPPN, DPMN) complexes (see Table IV). For the DPPN-containing complexes, the signals assigned to the alkyl carbons α to the phosphorus appear as 1:2:1 triplets as expected for the proposed trans formulations.[29,30]

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Table IV. Carbon-13 Nuclear Magnetic Resonance Spectral Data[a,b]

compd	$\delta(C_\alpha)$	J_{PC}	$\delta(C_\beta)$	J_{PC}	$\delta(C_\gamma/C_{\gamma'})$[c]	J_{PC}	$\eta(C_1)$	J_{PC}	$\delta(C_2/C_6)$	J_{PC}	$\delta(C_3/C_5)$	J_{PC}	$\delta(C_4)$	J_{PC}
$Ph_2PCH_2CH_2CN$ (DPPN)	24.1 (d)	15.6	14.1 (d)	23.6	119.3 (d)	14.6	136.4 (d)	12.5	132.6 (d)	19.2	128.9 (d)	13.4	128.9 (s)	
$Ph_2PCH_2CH(CH_3)CN$ (DPMN)	33.3 (d)	16.6	23.0 (d)	20.5	122.4 (d)	6.8	136.9 (d)	12.7	132.6 (d)	19.5	128.7 (d)	12.7	128.8 (s)	
					19.2 (d)	9.8	136.8 (d)	11.7						
$PdCl_2(DPPN)_2$	22.3 (t)	30.6	12.7 (s)	0	118.5 (t)	18.9	127.9 (t)	47.8	133.5 (t)	11.9	128.8 (t)	10.3	131.4 (s)	
$PdBr_2(DPPN)_2$	25.0 (t)	31.3	13.2 (t)	5.9	118.5 (t)	18.6	128.9 (t)	48.8	133.7 (t)	11.7	128.8 (t)	9.8	131.4 (s)	
$PdCl_2(DPMN)_2$	30.0 (t)	29.3	21.7 (s)	0	121.6 (t)	5.6	129.4 (t)	41.5	134.5 (t)	12.8	128.7 (t)	10.5	131.6 (s)	
					20.5 (t)	8.8	129.3 (t)	36.5	133.2 (t)	11.5			131.1 (s)	
							127.6 (t)	48.2						
							127.5 (t)	47.4						
$PdBr_2(DPMN)_2$[d]	32.6 (t)	30.2	22.6 (s)	0	121.6 (t)	5.1			134.6 (t)	12.7	128.6 (t)	10.4	131.5 (s)	
	32.5 (t)	30.5			20.5 (t)	9.6			133.2 (t)	11.5			131.0 (s)	
$Pd_2Cl_4(DPPN)_2$	23.9 (d)	37.7	12.8 (s)	0	118.0 (d)	19.6	125.8 (d)	58.7	133.1 (d)	10.0	128.2 (d)	12.1	132.6 (d)	3.3
$Pd_2Br_4(DPPN)_2$	26.7 (d)	38.1	13.4 (d)	2.9	118.0 (d)	19.5	127.3 (d)	56.6	133.3 (d)	10.7	129.3 (d)	11.7	132.6 (d)	2.9
$PdCl_2(DPPN \cdot MeOH)$[d,e]									133.0 (d)	8.8	128.0 (d)	11.7	131.2 (d)	2.8

[a] In $CDCl_3$ relative to $SiMe_4$. Alkyl- (including CN) and phenyl-group carbons are labeled C_α–C_γ and C_1–C_6, respectively, with C_α and C_1 designating the carbons bonded to phosphorus. Coupling constants are expressed in hertz. [b] J_{PC} represents $|^nJ_{PC} + {}^{n+2}J_{PC}|$ in the PdX_2L_2 complexes. [c] C_γ and $C_{\gamma'}$ are the signals assigned to the CN and CH_3 resonances, respectively. [d] Values are omitted for the signals that were not intense enough to assign with certainty. [e] DPPN·MeOH = $Ph_2P(CH_2)_2C(OCH_3)NH$.

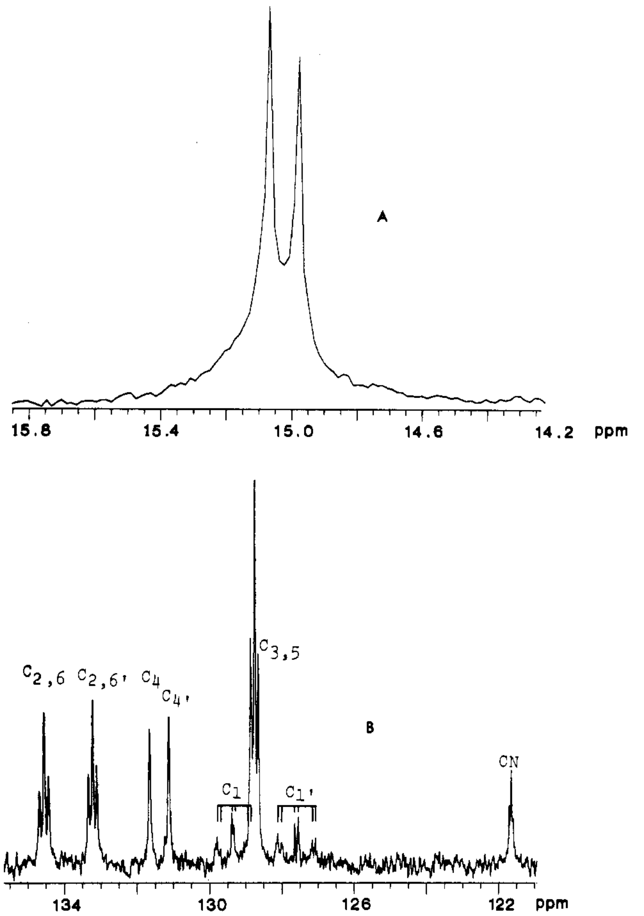

Figure 1. $^{31}P\{^1H\}$ (A) and $^{13}C\{^1H\}$ (B) NMR spectral data for $PdCl_2[Ph_2PCH_2CH(CH_3)CN]_2$.

Similarly, three of the four phenyl carbon resonances are also triplets. As indicated above, however, the spectra from the DPMN-containing complexes are consistent with spectroscopically identifiable diastereomers. Specifically, as shown in Figure 1 and Table IV, the two sets of peaks assigned to both C_2/C_6 and C_4 in $PdCl_2(DPMN)_2$ reflect the magnetic nonequivalence of the diastereomers. In addition, assuming that two peaks are under the signal assigned to C_3, the chloride–DPMN complex displays two doublets of triplets that are assigned to the ipso carbon, C_1 (see Figure 1). This pattern indicates that the diastereotopic C_1 carbons in the diastereomers are also magnetically distinguishable. For the bromide-containing complex, the C_1 carbon signals have not been detected in any of the spectra recorded. The other phenyl carbons, however, show patterns that are similar to those for the chloride-containing complex.

The $^{13}C\{^1H\}$ NMR data observed in the alkyl region for the DPMN-containing complexes are also presented in Table IV. In the spectra recorded for this study, only the $PdBr_2(DPMN)_2$ complex provides ^{13}C NMR signals consistent with distinguishable diastereomers. The pattern assigned to C_1 consists of two sets of triplets, which are separated by only 0.1 ppm. Further, the CN carbon signals of all these PdX_2L_2 complexes appear at higher field (ca. 0.8 ppm) than those in the free ligands. In contrast, shifts of 4.5 ppm to lower field have previously been observed for nitriles coordinated to palladium(II).[31]

Dimeric Complexes, $[PdX_2L]_2$. The reaction of DPPN, DPMN, or DPBN (L) with PdX_2 in a 1.0:1.1 mole ratio yields orange-red complexes of stoichiometry $[PdX_2L]_n$. As expected, the reaction of Na_2PdBr_4 with $PdBr_2[Ph_2P(o\text{-}C_6H_4CN)]_2$ provides an analogous product. The DPPN and DPMN complexes are more soluble in both benzene and chlorinated solvents than the DPBN-containing complexes. With chloroform at ambient conditions, for example, saturated solutions of $[PdCl_2(DPPN)]_n$ and $[PdBr_2(DPBN)]_n$ are ca. 15% and 0.3% by weight, respectively.

Molecular weight measurements have been obtained for $[PdX_2(DPPN)]_n$ (X = Cl, Br) and $[PdBr_2(DPBN)]_n$ giving values corresponding to dimers (see Table I). Measurements on dilute $[PdCl_2(DPPN)]_2$ solutions, however, consistently provided molecular weights of ca. 750 rather than 831, the value calculated for a dimer. Values from 811 to 850 were consistently obtained on solutions with at least 10 mg of sample/mL of $CHCl_3$.

Both halogen and ligand bridges are likely structural possibilities for these Pd(II) dimers. Halogen-bridged dimers of type *sym-trans*-$Pd_2X_4L_2$ in which the L groups are phosphines are numerous, and their chemical and spectral properties are well established.[32,33] Though less numerous, ligand-bridged dimers have been reported for bidentate phosphines containing long backbone chains. For example, $[Cl_2Pd(t\text{-}Bu)_2P(CH_2)_{10}P(t\text{-}Bu)_2]_2$ has been shown to be bridged by trans-spanning phosphines.[34] As noted above, bridging through the phosphorus and nitrogen lone pairs has been reported previously for both DPPN and DPBN in complexes of stoichiometry $Re_2(CO)_6L_2X_2$ (X = Cl, Br).[10,11] For these Re com-

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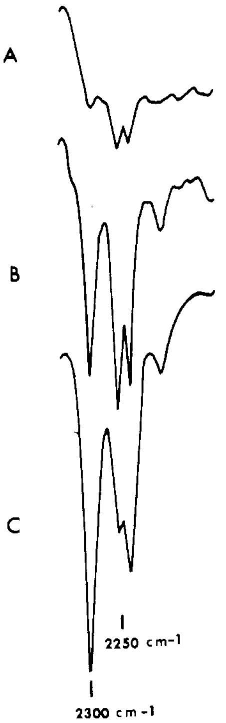


Figure 2. IR spectral data in the ν(CN) region for $[PdCl_2[Ph_2P(CH_2)_2CN]]_2$, recorded in $CHCl_3$ (A = 25 mg/mL; B = 200 mg/mL) and in a KBr pellet (C).

plexes, ν(CN) bands are observed at ca. 2300 cm^{-1}, which is in the range expected for end-on coordinated nitriles.[2,35]

The IR spectra for the $[Pd(DPBN)X_2]_2$ complexes suggest that both are halogen bridged. Both provide ν(CN) bands near 2225 cm^{-1}, which is consistent with free, rather than coordinated, nitrile groups. Bands at 355, 295, and 265 cm^{-1} are observed in the low-energy IR spectrum of the chloride-containing complex, the pattern expected for a sym-trans halogen-bridged complex.[32,33] A ν(PdBr) band was observed for the bromide-containing complex, at 275 cm^{-1}, but the remaining bands from a bridged structure are expected to be near or below 200 cm^{-1} and to be undetectable in the spectra recorded for this study.

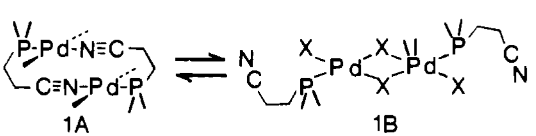
In contrast, the DPPN-containing complexes provide IR spectra that display ν(CN) bands at 2240, 2260, and 2305 cm^{-1} for both the chloride- and bromide-containing complexes. The positions of the former two bands correspond to those observed for the uncoordinated nitrile groups in the free ligands and the $PdX_2(DPPN)_2$ complexes, while the latter corresponds to the position expected for end-on coordinated nitrile groups.[2,35] Both the procedure used to record the spectra and the temperature affect the relative ν(CN) band intensities obtained from these complexes. When recorded in a Nujol mull, KBr pellet, or saturated $CHCl_3$ solution, the 2305-cm^{-1} band is more intense than the bands at 2245 and 2265 cm^{-1}. As shown in Figure 2, however, the spectrum obtained from a dilute $CHCl_3$ solution (2.5 mg/mL) displays only a very weak band at 2305 cm^{-1}. Further, when the spectrum is recorded in $CHCl_3$, decreasing the temperature also causes the intensity of the 2300-cm^{-1} band to increase relative to that of the bands at 2265 and 2245 cm^{-1}. In addition, the low-energy IR spectrum of $[PdCl_2(DPPN)]_2$ displays a strong band near 350 cm^{-1} with weaker bands near 300 and 270 cm^{-1}, a pattern consistent with a halogen-bridged structure.[32,33]

The ^{31}P NMR spectra of both $[PdCl_2(DPPN)]_2$ and $[PdBr_2(DPPN)]_2$ have been recorded at several temperatures between ambient probe temperature and 206 K. At ambient conditions, single peaks are observed at 29.0 and 30.7 ppm for the chloride and bromide complexes, respectively, providing, in turn, coordination chemical shifts ($\Delta\delta$ values) of 45.3 and 47.0 ppm. Both of these values are approximately 1.5 times larger than those obtained for the corresponding *trans*-$PdX_2(DPPN)_2$ complexes. This factor of 1.5 is similar to the values of 1.4 and 1.5 obtained when the chemical shifts from the halogen-bridged *sym-trans*-$[PdCl_2L]_2$ complexes are divided by those from the corresponding *trans*-$PdCl_2L_2$ (L = PPh_2Me, PPh_2Et) species.[29,36,37]

Two ^{31}P NMR signals are observed below 230 and 250 K for $[PdCl_2(DPPN)]_2$ and $[PdBr_2(DPPN)]_2$, respectively. The lower field signals, which are the more intense, remain sharp throughout the temperature range whereas the higher field signals are initially broad but sharpen as the temperature is lowered. At 213 K (X = Cl) and 206 K (X = Br) the areas of the peaks (low field:high field) are 2.0:1.0 and 2.6:1.0, respectively. At 223 K (X = Cl) and 226 K (X = Br) the ratios are 2.6:1.0 and 4.4:1.0, respectively. The chemical shift differences between the signals are 3.14 ppm (X = Cl; T = 213 K) and 5.13 ppm (X = Br; T = 206 K), which are larger than the 0.90-ppm difference observed for the $PdCl_2(DPMN)_2$ diastereomers but are less than the typical differences between the signals for the trans and the corresponding sym-trans complexes.[36,37] Both signals, however, are not only in the range expected for sym-trans complexes but also in the range predicted for a ^{31}P NMR signal for a phosphorus trans to a N-donor ligand.[29,37]

The ^{13}C NMR data for $[PdX_2(DPPN)]_2$ (X = Cl, Br) are summarized in Table IV. For both, the signals from the aliphatic and aromatic carbons labeled C_α and C_4, respectively, are at lower field by ca. 1.5 ppm relative to the corresponding signals from monomeric complexes with trans coordination. Pregosin has noted the chemical shift dependence of both C_α and C_4 on the trans ligand and has reported similar shifts for palladium(II) complexes with bridging halogens or amines trans to a phosphine.[29] Compared to those for the monomeric trans complexes, the CN carbon signals are also observed at lower field by ca. 0.5 ppm but are still at higher field than the signal observed for the free ligand. As noted previously, coordination through the CN carbon is expected to shift this signal to lower field.[31]

In view of the data presented above, it is proposed that these $Pd_2X_4(DPPN)_2$ complexes consist of ligand- and halogen-bridged species (**1A**,**B**) that interconvert rapidly on the NMR time scale.



1A 1B

As shown, the proposed ligand-bridged structure is trans coordinated, with the palladium atoms located over the π cloud of the adjoining CN group. This trans structure is preferred because the ^{31}P and ^{13}C NMR signals are in the range expected for phosphine groups trans to ligands which have a trans influence that is lower than that of a terminal halogen. Further, the IR spectrum of the chloride complex always shows a sharp band at ca. 350 cm^{-1}, which is consistent with the proposed trans arrangement. Finally, also in accord, the trans-coordinated dimer can be constructed with CPK models. The resulting dimer is rather rigid and must be constructed with the offset, face-to-face configuration shown.

The ν(CN) bands observed near 2300 cm^{-1} could also arise if halogen-bridged dimers polymerized through the uncoordinated CN groups as observed for $NiX_2[P(CH_2CH_2CN)_3]_2$.[38] Assuming intact halogen bridges, polymerization of this type would result in five- or six-coordinated structures and larger molecular weight values than those observed. For this reason and the fact that no electron absorption bands were observed in the (20–25) × 10^3 cm^{-1} region,[39,40] the dimeric formulation presented above is favored.

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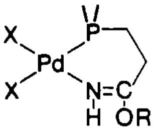
These $Pd_2X_4L_2$ complexes readily react with methanol or ethanol to provide yellow complexes that are sparingly soluble in organic solvents. As indicated in the Experimental Section, $PdCl_2[Ph_2P(o\text{-}C_6H_4C(OC_2H_5)NH)]$ has also been obtained from the reaction between H_2PdCl_4 and $PdCl_2[Ph_2P(o\text{-}C_6H_4CN)]_2$ in ethanol. The analytical and spectroscopic data (see Tables I and II) from the isolated complexes are entirely consistent with monomeric complexes containing chelating phosphine–imidate (phosphine–imino ether) ligands (**2**). Specifically, all IR spectra display strong bands in the ν(C═N) region and weak bonds in the ν(NH) region at ca. 3330 cm^{-1}, the range expected for N-coordinated imidate groups.[41] Further, as expected for cis coordination,[32,42] two ν(PdCl) bands are observed at ca. 350 and 280 cm^{-1} for the chloride-containing complexes.



2

Facile nucleophilic attack on organonitrile groups that are either coordinated to, or held proximate to, transition metals is well documented.[2] It has been reported, for example, that rate data from the reaction of amines with the CN group in the ligand-bridged complex $[(PPh_3)_2Pt(o\text{-}CH_2C_6H_4CN)]_2^{2+}$ indicate that the attack occurs via a $[(PPh_3)_2Pt(\text{amine})(o\text{-}CH_2C_6H_4CN)]^+$ five-coordinated intermediate in which the nitrile group is side-on coordinated.[43] In contrast, it has been proposed that direct attack by ethanol on the end-on coordinated nitrile groups in $[(Ph_2PCHCHPPh_2)Pt(o\text{-}CH_2C_6H_4CN)]_2^+$ accounts for the rapid formation of $[(Ph_2PCHCHPPh_2)Pt(o\text{-}CH_2C_6H_4C(OC_2H_5)NH)]^+$.[44] Although the reaction may not be metal activated, it has also been reported that the uncoordinated nitrile group in $(NCCH_2PPh_2)Pd(Cl)(o\text{-}C_6H_4NMe_2)$ undergoes attack by the carbanion formed by reacting the halogen-bridged $L_2Pd_2Cl_2$ ($L = o\text{-}C_6H_4NMe$) with $[Ph_2PCHCN]^-$.[45]

As outlined above, most examples of metal-promoted reactions at nitrile carbons involve neutral or anionic nucleophiles and cationic complexes. The reactions reported herein clearly indicate that nitrile groups in formally neutral complexes can also be activated. Further, it is possible that the side-on coordination, shown in **1A**, activates the cyano group toward attack as suggested (vide supra) for $[(PPh_3)_2Pt(\text{amine})(o\text{-}CH_2C_6H_4CN)]^{+}$[43] and proposed initially by Clark.[46]

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Ball State University Faculty Research Grant program for support of this research. The assistance provided by John M. Risley and Greg L. Durst is gratefully acknowledged.

Registry No. $PdCl_2(DPPN)_2$, 96483-01-1; $PdBr_2(DPPN)_2$, 96483-02-2; $PdCl_2(DPMN)_2$ (isomer 1), 96483-03-3; $PdCl_2(DPMN)_2$ (isomer 2), 96554-68-6; $PdBr_2(DPMN)_2$ (isomer 1), 96483-04-4; $PdBr_2(DPMN)_2$ (isomer 2), 96554-69-7; $PdCl_2(DPBN)_2$, 96483-05-5; $PdBr_2(DPBN)_2$, 96483-06-6; $[PdCl_2(DPPN)]_2$, 96483-07-7; $[PdBr_2(DPPN)]_2$, 96483-08-8; $[PdCl_2(DPBN)]_2$, 96483-09-9; $[PdBr_2(DPBN)]_2$, 96483-10-2; $PdCl_2[Ph_2P(CH_2)_2C(OCH_3)NH]$, 96483-11-3; $PdBr_2[Ph_2P(CH_2)_2C(OCH_3)NH]$, 96483-12-4; $PdCl_2[Ph_2P(CH_2)_2C(OC_2H_5)NH]$, 96483-13-5; $PdCl_2[Ph_2P(o\text{-}C_6H_4C(OCH_3)NH)]$, 96483-14-6; Na_2PdCl_4, 13820-53-6; Na_2PdBr_2, 50495-13-1; DPPN, 5032-65-5; DPMN, 96483-00-0; DPBN, 34825-99-5; acrylonitrile, 107-13-1; diphenylphosphine, 829-85-6; methacrylonitrile, 126-98-7.

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A Chemical, FT-IR, and EXAFS Study of the Interaction between $HFe_4(CH)(CO)_{12}$ and Partially Dehydroxylated Alumina

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Received November 16, 1984

The initial reaction of $HFe_4(CH)(CO)_{12}$ with partially dehydroxylated alumina produces $[HFe_4(C)(CO)_{12}]^-$, which is bound to the surface. Evolution of CO occurs slowly by extensive loss of CO from a small number of cluster molecules. This process leads to the coexistence of intact $[HFe_4(C)(CO)_{12}]^-$ plus an iron or iron carbide like species. In keeping with this interpretation, the supported material displays activities for the reduction of CO and the hydrogenation of benzene and product distributions that are typical of iron metal.

Introduction

The preparation of heterogeneous catalysts by the interaction of transition-metal carbonyl complexes with solid supports, especially inorganic oxides, has received widespread attention.[1-3] At low metal carbonyl loadings, the potential exists for the preparation of heterogeneous catalysts with discrete metal sites equivalent in nuclearity to the starting metal carbonyl cluster.

The chemisorption of a metal carbonyl complex on a metal oxide, however, is often much more complicated, resulting in a surface species of different nuclearity. A well-known example is the reaction of dinuclear or tetranuclear rhodium carbonyl complexes with alumina to yield $Rh_6(CO)_{16}$.[4-6] Evidence also has been presented for the formation of large osmium clusters upon

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