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Reactions of Phosphine–Nitrile Ligands: the formation of Phosphine–Amine and Phosphine–Imidate Complexes of Tungsten Carbonyl from 3(Diphenylphosphino)propionitrile and 3(Diphenylphosphino)2-methylpropionitrile

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Abstract

Reactions of $W(CO)_6$ and $NaBH_4$ with the phosphine–nitrile ligands $Ph_2PCH_2CH_2CN$ or $Ph_2PCH_2CH(CH_3)CN$ in hot ethanol or propanol for limited reaction times provide mixtures of the corresponding phosphine–imidate and phosphine–amine complexes of the stoichiometry $(CO)_4WL$. Longer reaction times provide, in high yield, only the phosphine–amine complexes. Proton-decoupled carbon-13 NMR data from $(CO)_4W[Ph_2PCH_2CH(CH_3)CH_2NH_2]$ are consistent with a locked, six-membered chelate ring in which the methyl group occupies an equatorial position. The NH and NH_2 donor groups in the $W(CO)_4L$ complexes are displaced upon reaction with $PhP(CH_3)_2$ providing mixtures of *cis* and *trans* $(CO)_4WLL'$ complexes.

Introduction

A wide variety of phosphine–nitrile ligands of the general type $R_xP[(CH_2)_nCN]_{3-x}$ (n = 1–4) have been shown to be readily obtainable by, for example, Arbuzov, [1–3] and Michael-like reactions [4]. Of those reported, the ligand properties of $Ph_2PCH_2CH_2CN$ (DPPN) [4–6] and $P[CH_2CH_2CN]_3$ [7, 8] have been studied to the greatest extent, and, for these, bidentate bridging, bidentate chelating and monodentate bonding modes have been proposed on the basis of spectroscopic data. In addition, some of the well-established CN-group reactions have been used to obtain other functionalities. In a recent paper, for example, Kyba reported that $HP(CH_2CH_2CN)_2$ is converted to the corresponding acid and alcohol by, in turn, hydrolysis and reduction reactions [9]. Along the same line, Meek has shown that $Ph_2P(CH_2)_3P(Ph)(CH_2)_3NH_2$ is obtained from the $LiAlH_4$ reduction of the nitrile-containing precursor [10]. Finally, we have reported that phosphine–imidate complexes are formed if complexes of the type $(PdX_2DPPN)_2$ are treated under mild conditions with alcohol [5]. Here we describe the preparation of both phosphine–imidate and phosphine–amine complexes of W(0) from mixtures of $Ph_2PCH_2CH(CH_3)CN$ (DPMN) or DPPN along with $W(CO)_6$ and $NaBH_4$ in alcohols.

Experimental

Tungsten hexacarbonyl, triphenylphosphine and dimethylphenylphosphine (all from Strem Chemicals, Inc.) along with sodium borohydride (Aldrich Chemical Company) were obtained from the indicated sources and used as received. Prior to use, ethanol and propanol were distilled from magnesium ethoxide and sodium, respectively. 3(diphenylphosphino)propionitrile (DPPN) and 3(diphenylphosphino)2-methylpropronitrile (DPMN) were prepared as described previously [5]. All glassware was dried at 130 °C prior to use, and all reactions were carried out in a nitrogen atmosphere.

Infrared spectra were recorded on a Beckman 4250 spectrophotometer which was calibrated with polystyrene. The $^{31}P[^1H]$ and $^{13}C[^1H]$ spectra were obtained with a Varian FT-80A instrument.

Elemental analyses (see Table I) were performed by Midwest Microlab, Ltd., Indianapolis, Ind. Silica gel products (coated plastic strips and flash-grade powder) were obtained from J. T. Baker. Unless noted otherwise, dichloromethane was used as the chromatographic elutant.

Syntheses

$(CO)_4W[Ph_2PCH_2CH(R)CH_2NH_2]$ (R = H, CH_3)

In a typical preparation, nitrogen was bubbled for 0.2 h through 150 ml of refluxing absolute ethanol. Tungsten hexacarbonyl (3.52 g, 10.0 mmol), $Ph_2PCH_2CH(CH_3)CN$ (2.54 g, 10.0 mmol) and $NaBH_4$ (2.28 g, 60.3 mmol) were added to the hot

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TABLE I. Analytical Data

Compound	Analyses (found/(calc.))			
	%C	%H	%N	%Cl
$(CO)_4W[(C_6H_5)_2PCH_2CH_2C(OC_2H_5)NH]$	43.25	3.53	2.26	–
	(43.40)	(3.47)	(2.41)	
$(CO)_4W[(C_6H_5)_2PCH_2CH_2C(OC_3H_7)NH]$	44.27	3.71	2.14	–
	(44.39)	(3.73)	(2.35)	
$(CO)_4W[(C_6H_5)_2PCH_2CH_2CH_2NH_2]\cdot\frac{1}{2}CH_2Cl_2$	40.09	3.22	2.03	5.43
	(40.27)	(3.29)	(2.41)	(6.10)
$(CO)_4W[(C_6H_5)_2PCH_2CH(CH_3)C(OC_2H_5)NH\cdot\frac{3}{4}CH_2Cl_2$	41.70	3.65	2.08	–
	(41.47)	(3.60)	(2.13)	
$(CO)_4W[(C_6H_5)_2PCH_2CH(CH_3)C(OC_3H_7)NH]$	44.99	3.97	2.52	–
	(45.34)	(3.97)	(2.30)	
$(CO)_4W[(C_6H_5)_2PCH_2CH(CH_3)CH_2NH_2]\cdot\frac{1}{4}CH_2Cl_2$	42.25	3.64	2.48	3.62
	(42.34)	(3.60)	(2.44)	(3.09)

ethanol and the mixture refluxed for 14 h. The ethanol was removed with a rotary evaporator, and the resulting yellow solid was shaken with a mixture of 150 ml each of water and dichloromethane. The dichloromethane layer was separated and dried over anhydrous magnesium sulfate. The drying agent was removed by filtration, and the yellow solution evaporated to dryness to yield 5.49 g (99.2%) of yellow colored product.

Both products ($R = H$, CH_3) were crystallized from mixtures of dichhloromethane and hexane. For example, 0.50 g of the above product ($R = CH_3$) was dissolved under a nitrogen atmosphere in 12 ml of refluxing dichloromethane. Hexane, 2 ml, was added and the resulting solution heated to evaporate solvent until a slight cloudiness was observed. (The final volume was *ca.* 5 ml.) Yellow-colored crystals formed upon cooling the mixture to −10 °C. The yield was 0.39 g (78%). See Tables I and II for analytical and spectroscopic data, respectively.

Mixtures of $(CO)_4W[Ph_2PCH_2CH(R)C(OC_2H_5)$-$NH]$ *and* $(CO)_4W[Ph_2PCH_2CH(R)CH_2NH_2]$ $(R = H, CH_3)$

In a typical reaction, $W(CO)_6$ (3.58 g, 10.2 mmol), $Ph_2PCH_2CH_2CN$ (2.41 g, 10.1 mmol) and $NaBH_4$ (2.28 g, 60.3 mmol) were added to 150 ml of hot ethanol that had been treated as described above. The mixture was refluxed for 4 h at which time TLC analyses of the mixture indicated two yellow spots ($R_f = 0.70$, 0.50) of approximately equal intensity. The reaction mixture was then treated as described above. The yellow solid that was obtained weighed 5.10 g. Flash chromatography (70% dichloromethane, 30% hexane) was used to isolate the products. Typically, 0.8 g each of the pure imidate (TLC $R_f = 0.70$) and amine (TLC $R_f = 0.50$) products were obtained from a 2.0 g sample of the mixture.

Mixtures of $(CO)_4W[Ph_2PCH_2CH(R)C(OC_3H_7)$-$NH]$ *and* $(CO)_4W[Ph_2PCH_2CH(R)CH_2NH_2]$ $(R = H, CH_3)$

In a typical reaction, $W(CO)_6$ (1.83 g, 5.2 mmol), $Ph_2PCH_2CH(CH_3)CN$ (1.26 g, 4.97 mmol) and $NaBH_4$ (1.14 g, 30.1 mmol) were dissolved in hot n-propyl alcohol that had been treated as described above for ethanol. The reaction mixture was stirred and maintained at 70 °C for 1.5 h. At that time, TLC analyses indicated the presence of two yellow spots ($R_f = 0.70$, 0.55) of approximately equal intensity. Following the reaction, 100 ml each of water and dichloromethane were added to the reaction mixture and the mixture shaken. The dichloromethane layer was separated, and the aqueous layer extracted with another 100 ml portion of dichloromethane. The dichloromethane fractions were combined, dried over anhydrous magnesium sulfate and evaporated with a rotary evaporator to yield 1.70 g of a yellow solid. As described above, flash chromatography was used to isolate the two components corresponding to the TLC spots. Both were crystallized from mixtures of dichloromethane and hexane.

The Reaction of $(CO)_4W[Ph_2PCH_2CH_2C(OC_2H_5)$-$NH$ *with* $NaBH_4$ *in ethanol*

Nitrogen was bubbled for 0.2 h through 50 ml of refluxing absolute ethanol. Sodium borohydride (0.16 g, 4.2 mmol) and $(CO)_4W[Ph_2PCH_2CH_2C(OC_2H_5)NH]$ (0.25 g, 0.43 mmol) were added to the hot ethanol and the mixture refluxed for 6 h. The solvent was removed with a rotary evaporator and the remaining yellow solid shaken with a mixture of 50 ml each of water and dichloromethane. The nonaqueous layer was then collected, dried over anhydrous magnesium sulfate, and evaporated to dryness yielding 0.21 g of yellow solid. A ^{31}P NMR spectrum of the product displayed two major peaks

TABLE II. Phosphorus-31 Nuclear Magnetic Resonance and Infrared Spectral Data

$(CO)_4WL$ Complexes	δP[a]	IR		
		$\nu(CO)$[b]	$\nu(NH)$[c]	νCN[c]
$Ph_2PCH_2CH_2C(OC_2H_5)NH$	16.6	2010(w) 1900(s,br) 1850(m)	3365	1640
$Ph_2PCH_2CH_2C(OC_3H_7)NH$	16.6	2015(w) 1900(s) 1895(s) 1845(m)	3360	1640
$Ph_2PCH_2CH(CH_3)C(OC_2H_5)NH$	14.4	2010(w) 1895(s,br) 1855(m)	3365	1640
$Ph_2PCH_2CH(CH_3)C(OC_3H_7)NH$	14.6	2010(w) 1900(s) 1895(s) 1850(m)	3360	1640
$Ph_2PCH_2CH_2CH_2NH_2$	6.1	2010(w) 1900(sh) 1885(s) 1860(m)	3340 3300	–
$Ph_2PCH_2CH(CH_3)CH_2NH_2$	8.5	2010(w) 1900(sh) 1885(s) 1860(m)	3340 3300	–
$(CO)_4WLL'$				
$Ph_2PCH_2CH(CH_3)C(OC_2H_5)NH$ $PhP(CH_3)_2$ (*cis*)	8.8 −26.9 (22.2)			
$Ph_2PCH_2CH(CH_3)C(OC_2H_5)NH$ $PhP(CH_3)_2$ (*trans*)	15.2 −20.5 (48.0)			
$Ph_2PPCH_2CH(CH_3)CH_2NH_2$ $PhP(CH_3)_2$ (*cis*)	9.3 −26.6 (22.4)			
$Ph_2PCH_2CH(CH_3)CH_2NH_2$ $PhP(CH_3)_2$ (*trans*)	14.8 −20.4 (48.0)			

[a] Recorded in $CD_3C(O)CD_3$; positive chemical shift values (ppm) are downfield from H_3PO_4; ${}^2J_{PP}$ coupling constant values are presented in parenthesis and expressed in Hz. [b] In cm^{-1}; recorded in $CHCl_3$. [c] Recorded as KBr pellets.

of approximately equal intensities at δ 16.6 and δ 6.1.

cis and trans-$(CO)_4W[Ph_2PCH_2CH(CH_3)CH_2NH_2][PhP(CH_3)_2]$

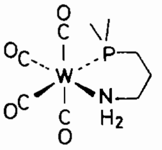
Nitrogen was bubbled for 0.5 h through 5 ml of deuterated acetone contained in a 50 ml round-bottomed flask. Dimethylphenylphosphine (125 μl, *ca.* 1 mmol) and $(CO)_4W[(Ph)_2PCH_2CH(CH_3)CH_2NH_2]$ (0.25 g, 0.45 mmol) were added to the solvent and the mixture refluxed for 48 h. The products were identified by a ${}^{31}P$ NMR spectrum (see Table II) which was obtained directly on the reaction mixture.

cis and trans-$(CO)_4W[Ph_2PCH_2CH_2C(OC_2H_5)NH])[PhP(CH_3)_2]$

These products were obtained by reacting $PhP(CH_3)_2$ (35 μl, *ca.* 0.3 mmol) with $(CO)_4W[(Ph)_2PCH_2CH_2C(OCH_2H_5)NH]$ (0.07 g, 0.1 mmol) in deuterated acetone as described above. Again, the products were identified by NMR measurements.

Results and Discussion

The reaction of a one-to-one mole ratio of $W(CO)_6$ with DPMN or DPPN and an excess of $NaBH_4$ in either dry ethanol or propanol for *ca.* 14 h provided air stable phosphine–amine complexes of type **1**.



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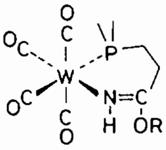

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As shown in Tables I and II, the ^{31}P NMR, IR and analytical data support this conclusion. With shorter reaction times, both ligands yielded, as evinced by TLC and NMR studies, mixtures of the phosphine–amine complex and another phosphine complex of tungsten carbonyl. The components of the mixtures were separated by flash chromatography and the additional compounds shown to be phosphine–imidate complexes, **2**. As expected, the phosphine–imidate complexes all provided IR spectra which displayed single bands of weak intensities in the ν(NH) region along with more intense bands in the ν(CN) region at 1640 cm^{-1} [5, 11]. Similarly, the phosphine–amine complexes displayed two bands near 3350 cm^{-1}, a pattern expected for coordinated primary amine groups [12]. Finally, all provided the expected patterns in the ν(CO) region [13].

All evidence we have obtained is consistent with the conclusion that the amine groups observed in these complexes arise from the imidate groups. First, nearly quantitative yields of phosphine–amine complexes are obtained upon prolonged heating of solutions which provide TLC and NMR evidence for the initial presence of both amine- and imidate-containing complexes. Second, phosphine–imidate complexes, isolated from column chromatography, have been reduced to the corresponding phosphine–amine complexes in ethanol. Finally, we have been unable to detect by $^{31}P[^1H]$ NMR measurements any phosphine–amine complexes analogous to those reported here when the reactions are carried out in dry THF rather than ethanol or propanol.

We are not aware of any other reports which describe the reduction of imidates either coordinated to, or held proximate to, formally neutral centers. Borch along with Crochet and Blanton have, however, clearly demonstrated that uncoordinated imidates are reduced by $NaBH_4$ to the corresponding amines, [14, 15]. It appears, therefore, that our experiments provide additional examples of reductions which are accomplished by first obtaining a reducible intermediate through a nucleophilic attack on the original substrate [16].

On the other hand, facile formation of imidate complexes from organonitriles and alcohols in the presence of transition metals has been reported for a wide variety of systems [17]. Although most reports have described attack on cationic complexes, the formally neutral $[PdX_2L]_2$ (X = Cl, Br; L = DPPN, DPMN) systems, as mentioned above, are reported to readily add methanol or ethanol to yield the corresponding monomeric, phosphine–imidate complexes [5]. Both side-on [18, 19] and end-on [20] metal–nitrile interactions have been proposed to promote such reactions, even though the vast majority of studied metal–nitrile interactions are of the latter type [17].

For the reactions reported here, it is possible that the reactions proceed via hydride-bridged intermediates of the type $[(\mu\text{-H})W_2L_2(CO)_8]^-$ (L = phosphine-coordinated DPPN or DPMN) which lose H_2 in the presence of alcohol to form $LM(CO)_4$. A complex of the former type, $[(\mu\text{-H})(Ph_2PCH_3)_2Mo_2(CO)_8]^-$, has been characterized by X-ray crystallographic methods [21], whereas the $LM(CO)_4$ intermediates have been proposed [22, 23] to account for products observed upon reaction of phosphines with the dimeric hydride anions, $[\mu\text{-HM}_2(CO)_{10}]^-$ (M = Cr, Mo, W). Assuming that the ligand properties of DPPN and DPMN are dominated by the P(III) centers, the primary coordination sphere of a monomeric $W(CO)_4L$ unit could be completed with a solvent molecule or a side-on coordinated nitrile group. Either situation could account for the observed formation of the imidate complexes.

Proton decoupled ^{13}C data have been obtained for all compounds reported except $(CO)_4W[Ph_2PCH_2CH(CH_3)C(OC_3H_7)NH]$. Due to limited solubilities, CO carbon signals, as well as some of the ligand carbon signals were not observed in the spectra recorded for this study. Available aromatic-carbon region data are, however, presented in Table III along with assignments which were made on the basis of the usual intensity, coupling constant, and chemical shift rules [24, 25]. It is noteworthy that the DPMN-based complexes provided spectra which clearly indicated the presence of the nonequivalent phenyl groups. In addition, four signals have been observed in the aliphatic carbon region for $(CO)_4W[Ph_2PCH_2CH(CH_3)CH_2NH_2]$. Since unsymmetrical, potentially locked, single-phosphine-containing chelate rings are not common, these data will also be presented.

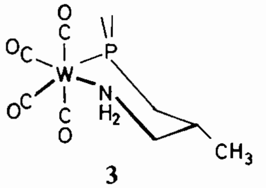
The four aliphatic carbon signals obtained for the $Ph_2PCH_2CH(CH_3)CH_2NH_2$-containing complex are observed as doublets centered at 54.9, 37.0, 32.3, and 23.6 ppm with coupling constants of 4.5, 19.4,

TABLE III. Phenyl Region $^{13}C[^1H]$ NMR Data[a]

	δC_1 (JPC) $\delta C_1'$ (JPC)	$\delta C_2/C_6$ (JPC) $\delta C_2'/C_6'$ (JPC)	$\delta C_3/C_5$ (JPC) $\delta C_3'/C_5'$ (JPC)	δC_4 (JPC) $\delta C_4'$ (JPC)
$(CO)_4W[Ph_2PCH_2CH_2C(OC_2H_5)NH]$	137.5(38.2)	132.4(11.5)	129.5(10.1)	130.5(1.9)
$(CO)_4W[Ph_2PCH_2CH_2CH_2NH_2]$	137.4(32.4)	133.1(11.6)	129.3(9.2)	130.6(1.9)
$(CO)_4W[Ph_2PCH_2CH(CH_3)C(OC_2H_5)NH]$	b	132.9(11.8)	129.5(9.4)	130.8(1.5)
		132.8(11.8)	129.4(9.5)	130.7(1.6)
$(CO)_4W[Ph_2PCH_2CH(CH_3)CH_2NH_2]$[c]	138.5(41.0)	133.1(11.9)	129.4(8.8)	130.7(1.2)
	137.5(34.1)	132.8(11.6)	129.2(9.3)	130.5(1.2)

[a] Ipso carbons are labeled C_1; recorded in deuterated acetone; chemical shift values are in ppm from TMS, used as an internal standard; coupling constants are reported in Hertz. [b] Signals attributed to these carbons were not observed. [c] Aliphatic-region signals were observed at δ 54.9(4.5), δ 37.0(19.4), δ 32.3(5.3) and δ23.6(13.3).

5.3, and 13.3 Hz, respectively. Based on coupling constants and phosphorus and nitrogen-induced deshielding parameters, the signals of nearly equal intensity at δ 54.9 and δ 37.0 have been assigned to the CH_2 groups adjacent to the NH_2 and Ph_2P moieties, respectively. Based on nuclear Overhauser effect arguments, the least intense doublet centered at δ 32.3 has been assigned to the methine carbon, which leaves the remaining doublet at δ 23.6 for the CH_3 carbon. The ^3JPC value for this latter signal is clearly much larger than that from the CH_2 group (13.3 *versus* 5.3 Hz) which is also γ to the phosphorus. The observed value (13.3 Hz) is, however, in the range expected for a carbon which has a P–C–C–C dihedral angle of *ca.* 180 °C [24]; the situation which is predicted for an equatorial carbon in a locked six-membered ring of the type shown in **3**.



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When free rather than coordinated, both the primary amine and imidate groups in these ligands could be useful for binding the phosphine center to solid supports. Since phosphines can replace nitrogen donor ligands on tungsten carbonyl centers, [26] we elected to react $(CO)_3W[Ph_2PCH_2CH_2C(OC_2H_5)NH]$ and $(CO)_4W[Ph_2PCH_2CH(CH_3)CH_2NH_2]$ with $PhP(CH_3)_2$ in order to determine if these chelate rings could be opened. The $^{31}P[^1H]$ spectra obtained from both following the reactions were similar in that eight new peaks (2 AX spin systems) were present, consistent with ring opening reactions yielding both *cis* and *trans* $(CO)_4WLL'$ complexes. For these, the area ratios of the higher-field to lower-field AX signals for each ligand are 2.5:1 and 3.5:1 for the phosphine–amine and phosphine–imidate complexes, respectively. As listed in Table II, the smaller-area AX patterns are assigned to the *trans* isomers on the basis of the coupling constant and chemical shift values [26, 27].

The observed *cis*:*trans* ratios are comparable to the value of 2.5 reported for the $(CO)_4WLL'$ product obtained from $(CO)_4W(Ph_2PC_2H_5)$(pyridine) and $PhP(CH_3)_2$ [26]. For this and related recently-reported products, the isomer ratios were shown to be dependent on the cone angles of L and L′ [26]. Given the ratios obtained, it appears that the sizes of the phosphine coordinated phosphine–amine and phosphine–imidate ligands are similar to $Ph_2PC_2H_5$.

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