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Registry No. I, 72905-42-1; II, 72983-35-8; III, 72937-78-1; IV, 72937-79-2; VI, 72937-80-5; VII, 72983-36-9; IX, 72905-31-8; X, 72905-32-9; trans-carboxylate $Co(L\text{-}His)_2^+$, 28696-52-8; trans-carboxylate $Co(L\text{-}Pyala)_2^+$, 72982-76-4; trans-imidazole $Co(L\text{-}His)_2^+$, 18744-92-8; trans-amino $Co(L\text{-}His)_2^+$, 24419-71-4; trans-amino $Co(L\text{-}Pyala)_2^+$, 72982-77-5; $Co(NO_3)_2$, 10141-05-6; $[Co(NH_3)_4CO_3]NO_3$, 15040-52-5; $[Co(NH_3)_6](NO_3)_3$, 10534-86-8; $Na_3[Co(CO_3)_3]$, 23311-39-9.

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Palladium(II) Thiocyanate Organophosphorus Complexes[1]

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A series of seven complexes of the type $L_2Pd(CNS)_2$ [$L = R_nP(C_6H_5)_{3-n}$, $n = 0-3$, R = methyl and benzyl] have been prepared and investigated for geometrical and linkage isomerism. The complexes have been characterized from physical properties, infrared spectroscopy, and ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopy. Most of the complexes are exclusively trans in $CDCl_3$ solution, the exceptions being $L = (C_6H_5)_3P$ and $(C_6H_5)_2PCH_3$ which exhibit both cis and trans isomers. Infrared integrated intensity ratio studies in chloroform indicate the predominance of N-bonded isomers in every case, while NMR shows the presence of other possible linkage isomers for various complexes. An NMR shift reagent, $Eu(fod)_3$, was used to facilitate identification of the different linkage isomers in solution. The interrelation of geometrical and linkage isomerism for this series of complexes, as well as the factors influencing such, is discussed.

Introduction

The ambidentate bonding capability of the thiocyanate ion has been attracting much attention for at least the last decade. This ambidentate nature has been interpreted in terms of Pearson's "soft-hard" concepts,[3] antisymbiosis effects,[4] and π bonding.[5,6] Whatever the rationale, the thiocyanate ion is a chemical probe of molecular environment in that it responds to steric and electronic stimuli by bonding either through sulfur, through nitrogen, or in a bridging fashion. Much effort[7-21] has been expended toward understanding the importance and function of these stimuli in relation to the thiocyanate bonding mode in transition-metal complexes.

In the past, nickel(II), palladium(II), and platinum(II) have been preferentially employed in the majority of studies of this bonding behavior. Among these transition metals there exists a potential for several geometries. Many studies[11,13,15,20,21] have had the constraint of a bidentate neutral ligand, the nature of which, however, prohibits geometrical isomerism. The results of these studies, while valid in their own right, tend to paint an imcomplete picture of the various influences on linkage isomerism in nickel triad thiocyanate complexes. The $L_2M(CNS)_2$ complexes, where L is a monodentate neutral ligand, have the capacity for geometrical isomerism, which we feel should influence the thiocyanate bonding mode. With the work described in this paper we attempt to tackle the question of the interrelation of linkage and geometrical isomerism and the factors influencing each in $L_2M(CNS)_2$ complexes, specifically when M = Pd(II) and L is a series of monodentate phosphines.

Experimental Section

Reagents and Physical Measurements. Chemicals were reagent grade and were used as received from the manufacturer or were synthesized as described below. All solvents, when necessary, were dried by standard procedures and were stored over Linde 4-Å molecular sieves. All reactions involving phosphines were conducted in a nitrogen atmosphere. Melting points were determined on a Mel-temp melting point apparatus and are uncorrected. Satisfactory elemental analyses were performed by Chemalytics, Inc., Tempe, Ariz. 85282.

Infrared spectra were obtained on a Perkin-Elmer 599 spectrophotometer. Samples were studied as Nujol mulls between CsBr plates or as chloroform solutions in NaCl cells. Integrated intensities of the CN stretching absorptions were determined by literature methods.[22] Proton, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR were recorded at 99.54, 25.00, and 40.26 MHz, respectively, on a JEOL FX-100 spectrometer in Fourier transform mode. Proton and carbon chemical shifts are relative to internal Me_4Si while phosphorus chemical shifts are reported relative to external 85% H_3PO_4. Saturated $CDCl_3$ solutions for NMR were

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Table I. Infrared Spectral Data for $L_2Pd(CNS)_2$ Complexes

L	mp, °C	state[a]	ν(CN), cm⁻¹	$\Delta\nu_{1/2}$, cm⁻¹	A^b	ISR[b]	δ(NCS),[c] cm⁻¹	ν(M-P), cm⁻¹	CNS bonding mode	geometry[d]
Bzl_3P	185	solid	2116	7		0.09	425	347	SCN	trans
		soln	2085	59	13.0				NCS	trans
Bzl_2PPh	226	solid	2107	14		0.23	421, 434	356	NCS	trans
		soln	2094	45	14.7				NCS	trans
$BzlPPh_2$	192	solid	2090	52		1.20	460, 469	357	NCS	trans
		soln	2088	53	14.0				NCS	trans
Ph_3P	234	solid	2085	40		1.54	masked	347	NCS	trans
		soln	2093	38	19.5				NCS	trans
$MePPh_2$	219	solid	2110	20		0.36	458	356	SCN	trans
		soln	2085	58	14.9				NCS	trans
Me_2PPh	146	solid	2090	58		0.92	427, 435	356	NCS	trans
		soln	2090	64	9.7				NCS	trans
Me_3P	193	solid	2115, 2080	NA[e]		NA	480, 472	305	mixed	trans
		soln	2116, 2095	45	11.2				mixed	trans

[a] Solid state Nujol mull; solution $CHCl_3$. [b] Integrated intensity (10^{-4} M^{-1} cm^{-2}); ISR is internal standard ratio relative to salicylic acid. Typical values for the different bonding modes may be found in ref 22. [c] ν(CS) (700–850 cm^{-1}) masked in all cases. [d] From appearance of spectrum. [e] NA indicates that satisfactory results could not be obtained; the reaction[38] of $K_2[Pd(SCN)_4]$ with $(CH_3)_3P$ in CH_3OH produces *trans*-$Pd(PMe_3)_2(NCS)_2$ which exhibits ν(CN) at 2092 cm^{-1} and an ISR of 3.61.

Table II. 99.54-MHz ^1H NMR Spectral Data for $L_2Pd(CNS)_2$ at 25 °C[a]

	CH_2 or CH_3 chem shift δ, line shape,[b] "J" (Hz)[c]		
L	$L_2Pd(NCS)_2$	$L_2Pd(NCS)(SCN)$	$L_2Pd(SCN)_2$
Bzl_3P	3.21, t, 6.4	3.32, t, 6.9	3.49, t, 6.0
Bzl_2PPh	3.42, cqt	3.56, cqt	3.82, cqt
$BzlPPh_2$	3.78, t, 7.6	3.94, t, 6.8	4.14, t
$MePPh_2$	2.23, t, 8.0 2.03, d, 18.0[d]		
Me_2PPh	1.90, ct		
Me_3P		1.63, t, 7.3	

[a] ^1H NMR resonances in the phenyl region are not reported; δ relative to Me_4Si internal standard. [b] d = doublet, t = triplet, ct = collapsed triplet, cqt = collapsed quartet of triplets. [c] "J" = $|^nJ_{PH} + {}^{n+2}J_{PH}|$. [d] The triplet is for the trans isomer and the doublet for the cis isomer.

prepared as previously described.[23] A lanthanide shift reagent, $Eu(fod)_3$, was used in a 2:1 complex:$Eu(fod)_3$ ratio.

Syntheses. 1. Ligands. The ligands were purchased from commerical sources or prepared by standard Grignard reactions and were purified by vacuum distillation.[24]

2. Complexes. The chloride complexes, L_2PdCl_2, were prepared by standard methods,[24] and the thiocyanato complexes were prepared from these by metathesis reactions with NaSCN. An example of a typical synthesis follows.

(Dithiocyanato)bis(tribenzylphosphine)palladium(II). To 0.7861 g (1.0×10^{-3} mol) of dichlorobis(tribenzylphosphine)palladium(II) in 25 mL of chloroform was added 0.1620 g (2.0×10^{-3} mol) of NaSCN which was dissolved in 10–15 mL of methanol. After being stirred for ca. 1 h, the solution was stripped of all solvent on a rotary evaporator, and the resulting solid was extracted with hot chloroform. After being filtered, this solution was reduced in volume to ca. 15 mL. The yellow crystals which volunteered were recrystallized from 1:1 $CHCl_3$:C_6H_6, washed with anhydrous diethyl ether, and vacuum dried, yielding 0.7410 g (89%) of product (mp 185 °C).

Results

The spectral data for this series of complexes are given in Tables I–IV. The complex $(Bzl_3P)_2Pd(CNS)_2$ will be discussed in detail as to the methods of structure elucidation. Since these criteria apply to the remaining complexes as well. their results will only be summarized. Thiocyanate is represented as CNS where it would be inappropriate or is not possible, to specify the metal–thiocyante linkage.

$(Bzl_3P)_2Pd(CNS)_2$. From the infrared data (Table I) this complex appears to be *trans*-$L_2Pd(SCN)_2$ in the solid state.

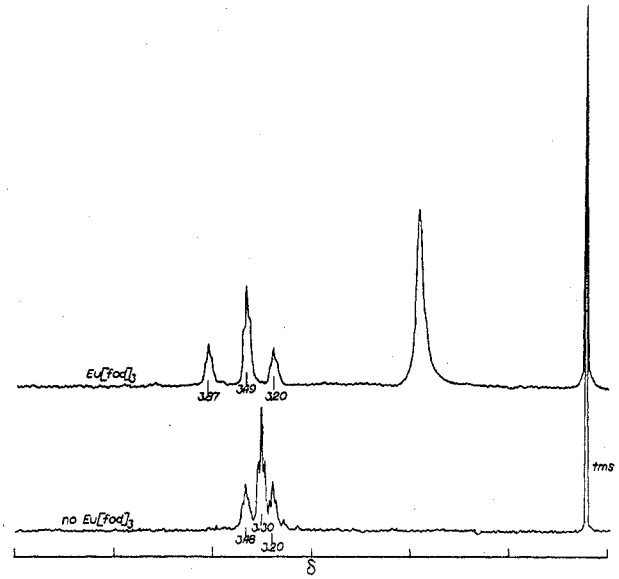

Figure 1. 99.54-MHz ^1H NMR spectrum of $(Bzl_3P)_2Pd(CNS)_2$ both with and without added $Eu(fod)_3$.

Linkage isomerization takes place upon dissolution in chloroform, as the solution IR integrated intensity data suggest that the predominant species is *trans*-$L_2Pd(NCS)_2$. The proton NMR results (Table II) shed more light on this situation, as three 1:2:1 triplets appear for the benzyl CH_2 resonances at δ 3.21, 3.32, and 3.49 with $|^2J_{PH} + {}^4J_{PH}| \simeq 6$–7 Hz for each triplet. This indicates the presence of three trans isomers in $CDCl_3$ solution. The $^{13}C\{^1H\}$ NMR (Table III) is less clear, showing two 1:2:1 triplets for the benzyl methylene carbons, all other resonances being singlets except for phenyl C_1, which gives the appearance of a 1:2:1 triplet with $|^2J_{PC} + {}^4J_{PC}| = 17$ Hz. The appearance of the $^{31}P\{^1H\}$ spectrum (Table III) supports the argument for three isomers in solution, giving three singlets having the following chemical shifts (relative intensities): δ 16.42 (0.29), *trans*-$L_2Pd(NCS)_2$; δ 14.78 (1), *trans*-$L_2Pd(NCS)(SCN)$; δ 11.67 (0.41), *trans*-$L_2Pd(SCN)_2$. These assignments were made with the help of an NMR shift reagent, $Eu(fod)_3$, whose effects are described forthwith.

Appreciable lanthanide-induced shifts have been observed[25] in the proton NMR spectra of organic and inorganic compounds containing S-bound thiocyanate groups but not in those

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Table III. 40.26-MHz $^{31}P\{^1H\}$ NMR Spectral Data for $L_2Pd(CNS)_2$ at 25 °C

L	$\delta(^{31}P)^a$ (rel % abund) trans-N_2	trans-NS	trans-S_2	cis-N_2	cis-NS	cis-S_2	% N	% S
Bzl_3P	16.42 (17.0)	14.78 (58.9)	11.67 (24.1)				46.4	53.6
Bzl_2PPh	16.72 (6.4)	16.89 (51.7)	15.06 (41.9)				32.3	67.7
$BzlPPh_2$	18.69 (24.1)	20.39 (54.6)	20.20 (21.3)				51.4	48.6
Ph_3P	22.90 (39.6)	18.84 (36.2)		28.08 (12.0)		25.68 (12.2)	69.7	30.3
$MePPh_2$	8.81 (11.0)	6.59 (1.3)	2.89 (1.7)	11.53 (73.5)		16.47 (12.5)	85.2	14.8
Me_2PPh	3.46 (100)						100.0	0.0
Me_3P^b		−10.74 (100)					50.0	50.0

[a] Positive sign indicates a downfield shift from 85% H_3PO_4 external standard. [b] Limited solubility precluded accurate percent abundance data.

Table IV. 25.00-MHz $^{13}C\{^1H\}$ NMR Spectral Data for $L_2Pd(CNS)_2$ at 25 °C[a]

L	$\delta(CH_2$ or $CH_3)$	"J"	$\delta(C_1)$	"J"	$\delta(C_{2,6})$	"J"	$\delta(C_{3,5})$	"J"	$\delta(C_4)$	"J"
					Benzyl					
Bzl_3P	29.7, t	22.0	132.6, t	17.0	130.0, s	0.0	129.1, s	0.0	127.5, s	0.0
	29.3, t	23.2								
Bzl_2PPh	29.4, t	22.0	132.6, t	12.2	130.2, t	4.9	128.7, s	0.0	127.3, s	0.0
	29.0, t	26.1								
$BzlPPh_2$	33.8, t	25.0	NO	NO	130.5, t	4.9	127.2, s	0.0	131.5, s	0.0
$MePPh_2$	12.7, t	30.0								
	14.0, d	31.8								
Me_2PPh	12.2, t	33.0								
Me_3P	13.2, t	31.8								
					Phenyl					
Bzl_2PPh			132.5, f	7.5	130.3, t	4.9	128.7, s	0.0	127.3, s	0.0
$BzlPPh_2$			NO	NO	133.4, t	12.2	128.4, t	NO	131.5, s	0.0
					133.7, t	12.2	128.7, t	NO		
Ph_3P			127.5, t	52.9	134.3, t	0.54	128.9, t	0.49	131.4, cm	NO
					134.5, t	0.54	129.2, t	0.49	131.6, cm	
$MePPh_2$			129.2, cm	NO	132.9, t	12.5	129.0, t	9.8	131.3, s	0.0
Me_2PPh			129.9, cm	NO	130.8, t	9.8	128.9, cm	NO	131.0, s	0.0

[a] Chemical shifts expressed in ppm relative to Me_4Si internal standard. s = singlet, t = triplet, f = five-line multiplet, cm = collapsed multiplet. "J" = $|^nJ_{PC} + {}^{n+2}J_{PC}|$. NO = not observed.

of compounds containing N-bound thiocyanates. We have extended the scope of this shift reagent to include $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR and have found similar behaviour to that observed in ^1H NMR.

In the proton NMR of $(Bzl_3P)_2Pd(CNS)_2$ (Figure 1), upon addition of $Eu(fod)_3$ the benzyl methylene proton resonance corresponding to the $L_2Pd(SCN)_2$ isomer moved downfield 0.39 ppm relative to its chemical shift without $Eu(fod)_3$ present. The $L_2Pd(SCN)(NCS)$ methylene resonance moved downfield 0.19 ppm relative to no $Eu(fod)_3$, while the $L_2Pd(NCS)_2$ resonance did not move. In the $^{13}C\{^1H\}$ spectrum in the presence of $Eu(fod)_3$, the apparent 1:2:1 triplet assigned to phenyl C_1 became three 1:2:1 triplets (figure 2), the $L_2Pd(SCN)_2$ triplet moving downfield by 0.3 ppm and the $L_2Pd(NCS)(SCN)$ triplet coming 0.02 ppm downfield of its original chemical shift. In the $^{31}P\{^1H\}$ NMR spectrum, the resonances behaved in a similar fashion to those of proton and carbon-13: the $L_2Pd(SCN)_2$ singlet moved downfield the farthest (0.62 ppm), followed by the $L_2Pd(NCS)(SCN)$ resonance (0.20 ppm), with the $L_2Pd(NCS)_2$ singlet unmoved. The relative percent abundances of the various isomers present (Table III) were determined from computer integration of the $^{31}P\{^1H\}$ spectrum. It was found that the relative amounts of each isomer did not change in the presence of shift reagent.

$(Bzl_2PPh)_2Pd(CNS)_2$. Infrared data indicate *trans*-$L_2Pd(NCS)_2$ in both the solid state and in chloroform solution. NMR conclusively shows the presence of the three possible trans isomers in solution, in a N_2:NS:S_2 ratio of 0.12:1:0.81.

$(BzlPPh_2)_2Pd(CNS)_2$. Infrared data indicate *trans*-$L_2Pd(NCS)_2$ in both the solid state and in solution. NMR shows the three possible trans isomers present in a N_2:NS:S_2 ratio of 0.44:1:0.39.

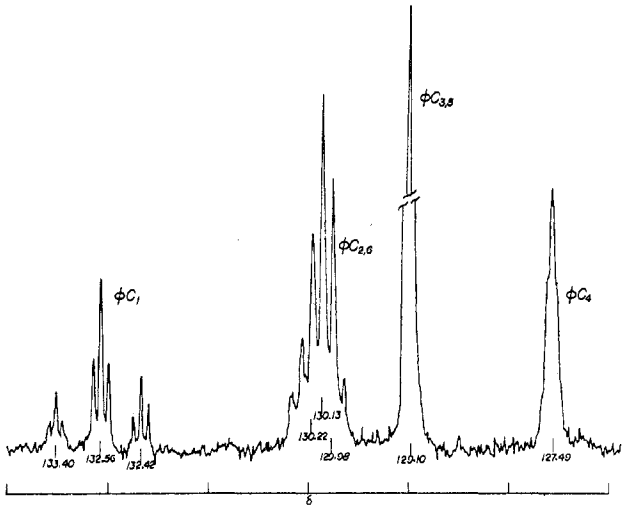

Figure 2. 25.00-MHz $^{13}C\{^1H\}$ NMR spectrum of the phenyl region of the complex $(Bzl_3P)_2Pd(CNS)_2$ in the presence of $Eu(fod)_3$.

$(Ph_3P)_2Pd(CNS)_2$. Consistent with the X-ray crystal structure[18] infrared data indicate *trans*-$L_2Pd(NCS)_2$ in both the solid state and in solution. NMR indicates geometrical isomerism as well as linkage isomerism by using the criteria for $^{31}P\{^1H\}$ previously delineated.[15,26,27] The relative isomer distribution is 1:0.91:0.30:0.31 trans-N_2:trans-NS:cis-N_2:cis-S_2.

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$(MePPh_2)_2Pd(CNS)_2$. Infrared data indicate *trans*-$L_2Pd(SCN)_2$ in the solid state and *trans*-$L_2Pd(NCS)_2$ in solution. NMR indicates geometrical as well as linkage isomerism. The relative isomer population is 0.15:0.017:0.023:1:0.17 trans-N_2:trans-NS:trans-S_2:cis-N_2:cis-S_2 (see ref 28).

$(Me_2PPh)_2Pd(CNS)_2$. Infrared data indicate that the complex is *trans*-$L_2Pd(NCS)_2$ in both the solid state and in $CHCl_3$ solution. NMR shows only one isomer in $CDCl_3$ solution, which is *trans*-$L_2Pd(NCS)_2$.

$(Me_3P)_2Pd(CNS)_2$. Infrared data for this complex were inconclusive as to the mode of linkage isomerism. A satisfactory internal standard ratio measurement could not be made on the solid complex. The solid state IR spectral appearance indicates that the complex is *trans*-$L_2Pd(NCS)(SCN)$. Solution IR data also indicate that the geometry is *trans*-$L_2Pd(NCS)(SCN)$. NMR measurements were made with difficulty as the complex has low solubility in $CDCl_3$. $^{31}P\{^1H\}$ NMR shows one isomer present, whose chemical shift moves downfield 0.18 ppm upon addition of $Eu(fod)_3$. A comparison of this behavior with that of the other complexes suggests that the solution structure is indeed *trans*-$L_2Pd(NCS)(SCN)$.

Discussion and Conclusions

It is known that the thiocyanate bonding mode is determined predominantly by steric effects,[11,29] electronic effects,[4,30] or a combination of the two.[10,12] A controversial aspect of the chemistry of nickel triad elements concerns the extent, if any, of retrodative metal–ligand π-bonding in square-planar bis(phosphine) complexes.[31] There have been a large number of papers rationalizing the bonding of thiocyanate ion with π-bonding arguments.[8,32] Recently, however, arguments for the dominance of steric effects in the determination of thiocyanate bonding mode have been put forth.[11,13] A preliminary investigation by us[28] has suggested that palladium(II) is schizophrenic toward the thiocyanate ion and that subtle changes in either steric or electronic effects will tip the balance and determine the thiocyanate bonding mode as well as the geometry of any individual complex.

The σ-donor ability for the series of phosphines in this work falls in the order $Me_3P > Me_2PPh > Bzl_3P > MePPh_2 > Bzl_2PPh > BzlPPh_2 > PPh_3$.[33] This ordering is supported for the most part by $\delta(^{31}P)$ for these compounds.[34,35] The relative size of these phosphines can be predicted from cone angle measurements[33] and are ranked $Bzl_3P > Bzl_2PPh > BzlPPh_2 > PPh_3 > MePPh_2 > Me_2PPh > Me_3P$. When the relative importance of steric and electronic effects are investigated, it is useful to consider the following points. (1) Palladium(II) is considered a "soft" metal center and should favor Pd–SCN bonding in the absence of other effects.[10] (2) Increasing the steric bulk of the ligand L should favor the formation of the trans-N-bonded isomer, while "electronic effects" should favor the cis-N-bonded isomer when L is a phosphine, due to antisymbiosis.[4] (3) Trans isomers of $L_2Pd(CNS)_2$ should predominate in $CDCl_3$ due to a major contribution of solvation terms to ΔH_{eq} and ΔS_{eq} for cis–trans isomerization.[36] (4) Trans influences and σ-donor–π-acceptor properties of the ligands will partly determine the internal bond energies of $L_2Pd(CNS)_2$ complexes. Even when taking all of these points into consideration, one should realize that the predominant isomer in solution and the most stable isomer in the solid state certainly need not be one and the same, due to differing solvation effects.[37]

The spectroscopic data for this series of complexes give no apparent trends regarding thiocyanate bonding mode based on either steric effects or electronic effects alone. There seems to be no regular ordering of $\delta(^{31}P)$ with respect to the linkage isomers of one phosphine complex when compared to those fo another, viz., the series of complexes of the benzyl phosphines. The factors leading to this apparent discrepancy are, at the moment, unclear. The difference in phosphorus electron density within a group of linkage isomers is apparently not a singular function of ligand basicity, ligand size, thiocyanate bonding mode, etc. It is interesting to note that the largest phosphine, Bzl_3P, gives no cis isomer (as expected), yet the smaller ligands in the series (except for $MePPh_2$) also give no cis isomer. The data support our earlier contention that small changes in electronic and steric effects play a large role in determining linkage and geometrical isomerism for palladium(II).[28] The appearance of "mixed-linkage" isomers in solution for most of the cases studied here also underlines palladium's schizophrenia toward the thiocyanate ion. It is readily apparent that many factors play a part in determining the geometry of these complexes, and it would be foolhardy to assume that one single factor controls the bonding pattern to the exclusion of the others for this series of complexes.

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Registry No. *trans*-$(Bzl_3P)_2Pd(NCS)_2$, 72893-60-8; *trans*-$(Bzl_3P)_2Pd(NCS)(SCN)$, 72893-61-9; *trans*-$(Bzl_3P)_2Pd(SCN)_2$, 72905-12-5; *trans*-$(Bzl_2PPh)_2Pd(NCS)_2$, 72893-62-0; *trans*-$(Bzl_2PPh)_2Pd(NCS)(SCN)$, 72893-63-1; *trans*-$(Bzl_2PPh)_2Pd(SCN)_2$, 72893-64-2; *trans*-$(BzlPPh_2)_2Pd(NCS)_2$, 72893-65-3; *trans*-$(BzlPPh_2)_2Pd(NCS)(SCN)$, 72893-66-4; *trans*-$(BzlPPh_2)_2Pd(SCN)_2$, 72893-67-5; *trans*-$(Ph_3P)_2Pd(NCS)_2$, 52194-15-7; *trans*-$(Ph_3P)_2Pd(NCS)(SCN)$, 72893-68-6; *cis*-$(Ph_3P)_2Pd(NCS)_2$, 41507-81-7; *cis*-$(Ph_3P)_2Pd(SCN)_2$, 72937-26-9; *trans*-$(MePPh_2)_2Pd(NCS)_2$, 67112-51-0; *trans*-$(MePPh_2)_2Pd(NCS)(SCN)$, 67112-50-9; *trans*-$(MePPh_2)_2Pd(SCN)_2$, 67063-54-1; *cis*-$(MePPh_2)_2Pd(NCS)_2$, 67063-58-5; *cis*-$(MePPh_2)_2Pd(SCN)_2$, 67063-59-6; *trans*-$(Me_2PPh)_2Pd(NCS)_2$, 72893-69-7; *cis*-$(Me_3P)_2Pd(NCS)(SCN)$, 72893-70-0; *trans*-$(Me_3P)_2Pd(NCS)(SCN)$, 72937-28-1; $(Bzl_3P)_2PdCl_2$, 43140-59-6; $(Bzl_2PPh)_2PdCl_2$, 68539-11-7; $(BzlPPh_2)_2PdCl_2$, 61046-58-0; $(Ph_3P)_2PdCl_2$, 13965-03-2; $(MePPh_2)_2PdCl_2$, 52611-08-2; $(Me_2PPh)_2PdCl_2$, 15616-85-0; $(Me_3P)_2PdCl_2$, 25892-38-0.

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