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Lewis Acid Adducts of *trans*-$PtHCN(P(C_2H_5)_3)_2$

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The reactions of several Lewis acids with *trans*-$PtHL_2CN$ [where $L = P(C_2H_5)_3$] gave stable adducts with the Lewis acid coordinated to the lone pair of electrons of the nitrogen atom. Variations in the coupling constant, ^1J(Pt–H), with the Lewis acid are used to establish a series of relative strengths of the Lewis acids. The acidity decreases roughly in the order $AlCl_3 > BAr_3 > BR_3 \sim CoCl_2 > AlAr_3 > ZnCl_2 > B(OAr)_3 > AlR_3 > AlR_2(OR)$. The reaction between 1 molar equiv each of $PtHL_2CN$, $PtHL_2Cl$, and $AgPF_6$ gives the complex $[PtHL_2CNPtHL_2](PF_6)$ which contains a cyanide bridging two $PtHL_2^+$ units.

Introduction

Lewis acids are very important cocatalysts for many industrial and laboratory reactions, a few of which are olefin polymerizations and dismutations, Friedel–Crafts alkylations, hydrogenations, and isomerizations. A study of the nature of the interaction between transition metals and Lewis acids is important in understanding the mechanisms of these processes.

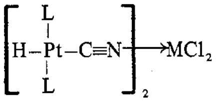
Kristoff and Shriver[1] examined the infrared spectra of a series of Lewis acid adducts of $(C_5H_5)Fe(CO)_2CN$ in which the acid was coordinated to the nitrogen lone pair of the cyanide. Because of the sensitivity of ν_{CO} to the nature of the group attached to the cyanide and because of negligible kinematic coupling of the CO stretching mode with other vibrations, they were able to arrange the Lewis acids according to their relative electron pair acceptor strengths.

More recently Cohen and Hoffman[2] recorded the ESR spectra of the complexes formed between the free radicals di-*tert*-butyl nitroxide or 2,2,6,6-tetramethylpiperidine-*N*-oxyl and group 4A Lewis acids. Variations in the nitroxide ^{14}N hyperfine coupling constants upon complexation were used to measure relative acceptor strengths of the Lewis acids.

In this paper we report a convenient method for measuring relative Lewis acidities toward a hydridoplatinum–cyano group using NMR spectroscopy.[3]

Results

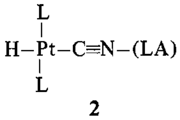
a. Preparation of the Complexes. The cyanide in *trans*-$PtHCNL_2$[4] [$L = P(C_2H_5)_3$] possesses a lone pair of electrons and reacts rapidly with $NiCl_2{\cdot}6H_2O$, $CoCl_2{\cdot}6H_2O$, and $ZnCl_2$ in acetonitrile to give 2:1 adducts, **1**. The nickel and cobalt complexes are stable indefinitely in the solid state but decompose slowly in solution. Trialkyl- and arylboron and -aluminum compounds react rapidly with $PtHCNL_2$ to form 1:1 adducts, **2**. These complexes were obtained as air-stable, white, crystalline solids.



$$\left[\mathrm{H{-}\overset{\displaystyle L}{\underset{\displaystyle L}{Pt}}{-}C{\equiv}N}\right]_2\!\!\rightarrow \mathrm{MCl_2}$$

1

M = Zn, Co, Ni



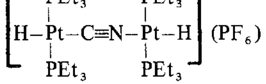
$$\mathrm{H{-}\overset{\displaystyle L}{\underset{\displaystyle L}{Pt}}{-}C{\equiv}N{-}(LA)}$$

2

The NMR spectra of the diamagnetic complexes are very similar. The phosphine ethyl resonances are complex and absorb downfield from tetramethylsilane. The platinum hydride resonance appears as a triplet due to coupling with the two equivalent ^{31}P nuclei ($I = {}^1/_2$, 100% natural abundance). The value of $^2J(H\text{–}Pt\text{–}P)$ is 15 Hz and does not vary from one complex to another. Each resonance is flanked by ^{195}Pt satellites ($I = {}^1/_2$, 33.8% natural abundance) and the magnitude of ^1J(Pt–H) varies with the Lewis acid. The NMR data obtained at 220 MHz are listed in Table I in order of decreasing ^1J(Pt–H).

The infrared spectra of the complexes show a very weak Pt—H stretching vibration around 2070 cm^{-1} and a strong C≡N vibration in the range 2050–2060 cm^{-1}. It is likely that these vibrations are strongly coupled to each other and are not pure.

The addition of $AgPF_6$ to an equimolar amount of *trans*-$PtHClL_2$ and *trans*-$PtHCNL_2$ in methanol gives a precipitate of AgCl and a clear colorless solution. Removal of the solvent gives a white crystalline complex. The NMR spectrum of the complex shows two nonequivalent platinum hydride resonances. The magnitudes of the Pt–H coupling constants (840 and 1100 Hz) are consistent with a hydride trans to C and N, respectively,[5] and support structure **3**.



$$\left[\mathrm{H{-}\overset{\displaystyle PEt_3}{\underset{\displaystyle PEt_3}{Pt}}{-}C{\equiv}N{-}\overset{\displaystyle PEt_3}{\underset{\displaystyle PEt_3}{Pt}}{-}H}\right](PF_6)$$

3

The electronic spectrum of $[PtHL_2CN]_2NiCl_2$ in benzene shows two bands in the visible region at 535 and 590 nm with molar extinction coefficients of 122 and 142 cm^{-1} m^{-1}. Similar spectra have been previously observed for tetrahedral nickel(II) complexes.[6] Generally they show a multiple band of approximately 10^2 cm^{-1} m^{-1} intensity which has been assigned to the $^3T_1(P) \leftarrow {}^3T_1(\nu_3)$ transition. The magnetic moment which was determined in benzene by the Evans technique[7] gave an effective magnetic moment, $\mu^{303}{}_{\text{eff}}$, of 3.4 μ_B. This moment also is consistent with a tetrahedral d^8 configuration.[8] We were unable to observe an ESR spectrum above liquid helium temperature suggesting a rapid electron spin relaxation. The NMR spectrum although slightly broadened gave chemical shifts comparable to those of the diamagnetic $ZnCl_2$ complex. We were unable to locate the hydride resonance. The NMR spectrum of $[PtHL_2CN]_2CoCl_2$ showed broadened phosphine ethyl resonances. A search upfield of tetramethylsilane did not reveal any hydride resonance; however, this resonance was located at 15.53 ppm *downfield* from TMS. Assuming that

Table I. The 220-MHz Data for Lewis Acid Adducts of $PtH(PEt_3)_2CN^a$

	Hydride		Phosphine		
Lewis acid	δ(Pt-H)	^1J(Pt-H)	$\delta(P\text{-}CH_2)$	$\delta(P\text{-}CH_3)$	Other resonances
$AlCl_3$	−6.79	860	1.48	0.83	
B(*p*-tol)$_3$	−7.51	854	1.42	0.78	$\delta(CH_3)$ 2.32
$B(C_6H_5)_3$	−7.69	852	1.85	1.04	
B(β-naph)$_3$	−7.78	851	1.13	0.56	
B(*o*-tol)$_3$	−7.68	848	1.38	0.73	$\delta(CH_3)$ 2.43
$B(CH_2CH_3)_3$	−7.64	844	1.54	0.88	$\delta(BCH_2)$ 0.99, $\delta(BCH_3)$ 1.46
$B(CH_2C_6H_5)_3$	−7.80	842	1.39	0.76	$\delta(BCH_2)$ 2.29
$CoCl_2$	+15.53	843	1.16	0.45	
$PtH(PEt_3)_2^+$	−8.13	840	1.91	1.11	δ(CN-PtH) 17.56, J(Pt-H) = 1100
$Al(C_6H_5)_3$	−7.40	836	1.45	0.82	
$B(C_6H_{11})_3$	−8.18	836	1.61	0.91	
$ZnCl_2$	−7.71	832	1.98	1.12	
$Al(CH_2CH_3)_3$	−7.50	830			
$B(OC_6H_5)_3$	−7.66	820	1.58	0.90	
$Al(CH_3)_3$	−7.59	816	1.66	0.99	$\delta(AlCH_3)$ 0.73
$Al(C_2H_5)_2(OC_2H_5)$	−7.38	814	2.02	1.29	$\delta(AlCH_2)$ 0.63, $\delta(AlCCH_3)$ 1.82, $\delta(OCH_2)$ 4.30, $\delta(OCCH_3)$ 1.66

[a] δ in ppm; J in Hz.

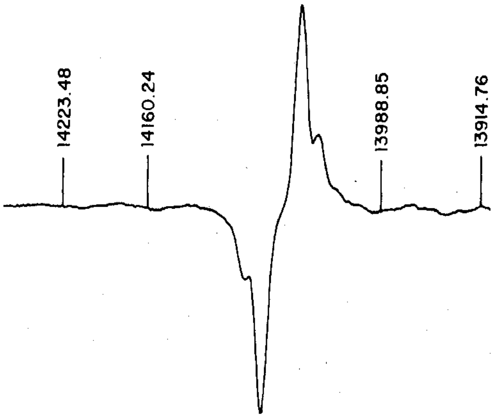


Figure 1. Electron spin resonance spectrum of *trans*-$PtH(PEt_3)_2$-$CN\cdot TiCl(C_5H_5)_2$ in toluene at 25 °C. Proton NMR field markers are in kilohertz.

the H–Pt–CN–Co unit is linear, the contact shift would be hyperfine rather than pseudocontact in origin, arising from electron delocalization from cobalt onto platinum. The electronic spectrum of the cobalt complex shows three absorption bands at 592, 615, and 664 nm with molar extinction coefficients of 570, 747, and 491 cm^{-1} M^{-1}, respectively. Generally tetrahedral cobalt(II) molecules[6] have a multiple band of approximately 10^2 cm^{-1} M^{-1} intensity near 625 nm due to the $^3T_1(P) \leftarrow {}^3T_1(\nu_3)$ transition. The magnetic moment of 4.3 μ_B (determined in benzene) is consistent with a tetrahedral d^7 electronic configuration.[8]

The reaction between $PtHL_2CN$ and $[(\eta^5\text{-}C_5H_5)_2TiCl]_2$[9] gave a bright green, air-sensitive, crystalline adduct $PtHL_2CN\cdot TiCl(C_5H_5)_2$, **4**. The magnetic moment ($\mu^{303}{}_{eff}$ = 1.6 μ_B) and visible spectrum are consistent with a d^1-electronic configuration. The ESR spectrum (Figure 1) shows hyperfine coupling to ^{195}Pt ($I = {}^1/_2$, 34% abundance) $\langle a_{Pt}\rangle$ = 7 G, and to $^{47,49}Ti$, $\langle a_{Ti}\rangle$ = ~12 G. The broadening in the main resonance (Figure 1) arises from hyperfine coupling to a nucleus with spin of $^1/_2$, 100% abundance. This coupling presumably is due to coupling of the electron from Ti, through the linear H–Pt–CN–Ti unit, to the hydride. This extended delocalization is presumably the same as that observed in the $CoCl_2$ complex.

Discussion

Organometallic complexes of platinum are particularly well suited for NMR studies because of the nuclear spin of the ^{195}Pt nucleus. For example ^1J(Pt–H) in the series of hydride complexes *trans*-$PtHL_2Z$ (where Z is an anionic or neutral ligand) varies from about 768 Hz for Z = CN^- to 1458 Hz for Z = acetone.[5] The one-bond coupling constant is thought to be dominated by the Fermi contact term.[5] Variations in ^1J(Pt–H) are then attributed mainly to variations in the s-electron density in the Pt–H bond. For good ligands there is considerable platinum 6s character in the Pt–Z bond and little Pt 6s character in the Pt–H bond. Therefore the coupling constant is small. As the bonding strength of Z decreases, less Pt s character is concentrated in the Pt–Z bond and more is concentrated in the Pt–H bond resulting in large values of ^1J(Pt–H). Thus, as the coupling constant increases, the Pt–Z bond weakens.[10]

In Table I the one-bond coupling constants are listed in decreasing values of ^1J(Pt–H). Although the range is small, 860–814 Hz, it can be seen that there is a definite weakening of the Pt–CN bond[10] as the Lewis acid is changed from $Al(C_2H_5)_2(OC_2H_5)$ to $AlCl_3$. If the complex is polarized as

$$\overset{\delta^+}{\text{H–Pt–C}}\overset{\delta^-}{\equiv\text{N}}\rightarrow\text{(LA)}$$

electron density will be withdrawn from the Pt–C bond as the strength of the Lewis acid increases. This argument refers only to the σ-bonding component of the Pt–CN bond. If there was a significant amount of π back-bonding from Pt to the cyanide, a stronger Lewis acid would strengthen the Pt–CN bond. However, considerable NMR data[5,11,12] and some of our unpublished work[13] would indicate that the cyanide is not a strong π-bonding ligand.

The Pt–H coupling, which presumably correlates with the relative strengths of the Lewis acids, decreases in roughly the following order: $AlCl_3 > BAr_3 > BR_3 \sim CoCl_2 > HPtL_2^+ > AlAr_3 > ZnCl_2 > B(OAr)_3 > AlR_3 > AlR_2(OR)$. This sequence differs somewhat from that of Shriver[1] in that he had $AlMe_3 > BMe_3$. These differences may be related to the fact that different Lewis bases were used to establish each series.

Small variations in ^1J(Pt–H) for the arylboranes may be due to steric effects.[10]

We may conclude that (1) coordination of a Lewis acid to the cyanide in $PtHL_2CN$ weakens the Pt–C bond and (2) variations in ^1J(Pt–H) provide a convenient and quick method for measuring relative Lewis acidities.

Experimental Section

trans-PtH $(P(C_2H_5)_3)_2Cl$ was prepared by a literature procedure[13] and the cyanide was prepared by metathesis using KCN. $(C_5H_5)_2TiCl$ was prepared from $TiCl_3$ and $Tl(C_5H_5)$ according to prescribed procedures.[9] All solvents were dried by passage through molecular sieves (Linde 4A). The aluminum and boron compounds were obtained commercially.

The 220-MHz NMR spectra were recorded on a Varian HR-220 spectrometer using $CDCl_3$ solutions with tetramethylsilane as internal reference.

Many of the complexes listed in Table I were isolated and the preparations are given below. In a few instances NMR spectra were recorded on solutions of the compound prepared by dissolving $PtHL_2CN$ in $CDCl_3$ and adding a stoichiometric amount of the Lewis acid.

Preparation of $[PtHL_2CN]_2CoCl_2$. A solution of $PtHL_2CN$ (0.523 g, 1.14 mmol) and $CoCl_2 \cdot 6H_2O$ (0.136 g, 0.57 mmol) in 50 ml of acetonitrile was refluxed for 1 h. The acetonitrile was removed by rotary evaporation to give a blue oil. Hexane was added and the oil crystallized within several minutes. The crystals were filtered off, washed with hexane, and air-dried. The solid was dissolved in the minimum amount of benzene and filtered, and hexane was added to give blue crystals; yield 0.490 g (83%); mp 145–148 °C. Anal. Calcd for $C_{26}H_{62}CoCl_2N_2P_4Pt_2$: C, 29.83; H, 5.97; N, 2.68; Cl, 6.77. Found: C, 29.93; H, 6.02; N, 2.91; Cl, 7.12. Visible spectrum (C_6H_6) (nm): 592 (570); 615 (747); 664 (491). Magnetic moment data (C_6H_6): $\chi_M = 7273.54 \times 10^{-6}$ emu/mol; $\mu^{303}{}_{eff} = 4.34\ \mu_B$.

Preparation of $[PtHL_2CN]_2ZnCl_2$. A solution of $PtHL_2CN$ (1.0 g, 2.18 mmol) and anhydrous $ZnCl_2$ (0.148 g, 1.08 mmol) in 50 ml of acetonitrile was refluxed for 2 h. The solution was filtered, the solvent was evaporated, and hexane was added to give a white solid. The hexane was decanted, benzene was added, the solution was filtered, and hexane was added dropwise to give white crystals. After cooling of the mixture in the refrigerator overnight, the crystals were filtered off and washed with pentane; yield 1.0 g (88%); mp 144–146 °C. Anal. Calcd for $C_{26}H_{62}Cl_2N_2P_4Pt_2Zn$: C, 29.65; H, 5.93; N, 2.66; Cl, 6.73. Found: C, 29.98; H, 5.85; N, 3.09; Cl, 7.05.

Preparation of $[PtHL_2CN]_2NiCl_2$. A solution of $PtHL_2CN$ (1.022 g, 2.22 mmol) and $NiCl_2 \cdot 6H_2O$ (0.265 g, 1.11 mmol) in 50 ml of acetonitrile was refluxed under nitrogen for 30 min. The solution became dark blue almost immediately. The solvent was removed by rotary evaporation to give a blue oil which was dissolved in dichloromethane and filtered. Hexane was immediately added to give dark blue crystals which were filtered off and dried in air; yield 1.0 g (85%); mp 146–148 °C. Anal. Calcd for $C_{26}H_{62}Cl_2N_2P_4Pt_2Ni$: C, 29.84; H, 5.97; N, 2.68; Cl, 6.77. Found: C, 30.19; H, 6.17; N, 2.93; Cl, 6.85. Visible spectrum (C_6H_6) (nm): 535 (122), 590 (142). Magnetic moment data (C_6H_6): $\chi_M = 4322.81 \times 10^{-6}$ emu/mol; $\mu^{303}{}_{eff} = 3.4\ \mu_B$. The complex may be prepared in air and the crystals appear to be stable indefinitely; however, solutions of this complex should not be exposed to the air for long periods of time since decomposition slowly occurs.

Preparation of $PtHCNL_2 \cdot B(C_6H_5)_3$. In the drybox a solution of $PtHL_2CN$ (0.770 g, 1.68 mmol) and $B(C_6H_5)_3$ (0.407 g, 1.68 mol) in the minimum amount of toluene was prepared. When all of the solids were in solution, hexane was added until the solution became cloudy. The flask was then cooled at −40 °C to give large white crystals. The crystals were filtered off and washed with pentane; yield 1.10 g (93%); mp 110–111 °C. Anal. Calcd for $C_{31}H_{46}BNP_2Pt$: C, 53.14; H, 6.62; N, 2.00. Found: C, 53.47; H, 6.62; N, 2.03.

Preparation of $PtHL_2CN \cdot B(CH_2C_6H_5)_3$. In the drybox $PtHL_2CN$ (1.0 g, 2.18 mmol) was dissolved in a small amount of toluene and solid $B(CH_2C_6H_5)_3$ (0.620 g, 2.18 mmol) was added. The boron compound rapidly dissolved to give a clear solution. Hexane was then added and the flask was cooled at −40 °C for 12 h to give large white crystals; yield 1.45 g (90%); mp 82–84 °C. Anal. Calcd for $C_{34}H_{52}BNP_2Pt$: C, 54.99; H, 7.06; N, 1.89. Found: C, 55.24; H, 6.88; N, 2.07.

Preparation of *trans*-$PtHL_2CN \cdot B(p\text{-}C_6H_4CH_3)_3$. To a solution of *trans*-$PtHL_2CN$ (0.527 g, 1.12 mmol) dissolved in toluene was added, as a solid, 0.32 g of tri-*p*-tolylboron. The solution was stirred until all of the solids had dissolved, pentane was added, and the solution was cooled to −40 °C overnight. White crystals separated. After 2 days they were filtered off and washed with pentane; yield 0.73 g; mp 132–134 °C. Anal. Calcd for $C_{34}H_{52}BNP_2Pt$: C, 54.99; H, 7.06; N, 1.89. Found: C, 55.38; H, 7.15; N, 2.18.

Preparation of *trans*-$PtHL_2CN \cdot BC_{30}H_{21}$. To a solution of *trans*-$PtHL_2CN$ (0.93 g) in toluene was added, as a solid (0.78 g, 1.99 mmol), tri-β-naphthylboron. The solution was stirred until the solids dissolved. Pentane was added and the flask was cooled to −40 °C overnight to give large white crystals. The crystals were filtered off and washed with pentane; yield 1.63 g; mp 159–192 °C. Anal. Calcd for $C_{43}H_{52}BNP_2Pt$: C, 60.70; H, 6.16; N, 1.65. Found: C, 60.37; H, 6.52; N, 1.85.

Preparation of *trans*-$PtHL_2CN \cdot B(C_6H_4\text{-}o\text{-}CH_3)_3$. To a solution of $PtHL_2CN$ (1.12 g, 2.39 mmol) in toluene was added, as a solid, 0.68 g of tri-*o*-tolylboron. The solution was stirred until all of the solids had dissolved. Pentane was added and the solution was cooled to −40 °C overnight to give large white crystals. The crystals were filtered off and washed with pentane; yield 1.62 g; mp 96–98 °C. Anal. Calcd for $C_{34}H_{52}BNP_2Pt$: C, 54.99; H, 7.06; N, 1.89. Found: C, 56.00; H, 7.01; N, 2.36.

Preparation of $PtHL_2CN \cdot BEt_3$. To a solution of *trans*-$PtHL_2CN$ (0.50 g, 1.09 mmol) in toluene was added 0.107 g of triethylboron. The solution was stirred for 15 min. Pentane was added and the solution was cooled to −40 °C overnight. Large white crystals separated. They were filtered off and washed with pentane; yield 0.23 g; mp 43–44 °C. Anal. Calcd for $C_{19}H_{46}BNP_2Pt$: C, 41.01; H, 8.33; N, 2.52. Found: C, 41.24; H, 8.25; N, 2.56.

Preparation of $(C_5H_5)_2TiCl(NC)PtHL_2$. To a suspension of $(C_5H_5)_2TiCl$ (0.466 g, 2.18 mmol) in toluene under an inert atmosphere was added $HPtL_2CN$ (1.0 g, 2.18 mmol). The solution rapidly turned yellow-green and after 20 min of stirring the solution was filtered. Pentane was slowly added and bright green crystals separated. The flask was cooled to −40 °C for 3 h, and the crystals were filtered off and washed with pentane; yield 1.30 g; mp 123–124 °C. Anal. Calcd for $C_{23}H_{41}ClNP_2PtTi$: C, 41.10; H, 6.15; N, 2.08; P, 9.22. Found: C, 40.89; H, 6.12; N, 2.08; P, 9.11. Visible spectrum (THF) (nm): 440 (563), 700 (62). Magnetic moment data (C_6H_6): $\chi_M{}^{cor} = 1032 \times 10^{-6}$ emu/mol; $\mu^{303}{}_{eff} = 1.6\ \mu_B$.

Preparation of $[HPtL_2CNPtHL_2](PF_6)$. To a solution of $HPtL_2Cl$ (0.50 g, 1.07 mmol) and $HPtL_2CN$ (0.49 g, 1.07 mmol) in methanol was added a solution of $AgPF_6$ (0.27 g, 1.07 mmol) in methanol. AgCl rapidly precipitated and after 20 min of stirring the solution was filtered to give a clear colorless solution. The solvent was removed to give white crystals; yield 0.95 g. Anal. Calcd for $C_{25}H_{62}F_6NP_5Pt_2$: C, 28.99; H, 6.03; N, 1.35. Found: C, 28.71; H, 6.09; N, 1.28.

Registry No. $PtH(PEt_3)_2CN \cdot AlCl_3$, 56731-32-9; $PtH(PEt_3)_2CN \cdot B(p\text{-tol})_3$, 56237-29-7; $PtH(PEt_3)_2CN \cdot B(C_6H_5)_3$, 55157-03-4; $PtH(PEt_3)_2CN \cdot B(\beta\text{-naph})_3$, 60594-99-2; $PtH(PEt_3)_2CN \cdot B(o\text{-tol})_3$, 56237-30-0; $PtH(PEt_3)_2CN \cdot B(CH_2CH_3)_3$, 56237-31-1; $PtH(PEt_3)_2CN \cdot B(CH_2C_6H_5)_3$, 56237-28-6; $[PtH(PEt_3)_2CN]_2CoCl_2$, 60594-93-6; $[HPt(PEt_3)_2CNPtH(PEt_3)_2](PF_6)$, 60594-96-9; $PtH(PEt_3)_2CN \cdot Al(C_6H_5)_3$, 60606-82-8; $PtH(PEt_3)_2CN \cdot B(C_6H_{11})_3$, 60594-98-1; $[PtH(PEt_3)_2CN]_2ZnCl_2$, 60594-94-7; $PtH(PEt_3)_2CN \cdot Al(CH_2CH_3)_3$, 60606-81-7; $PtH(PEt_3)_2CN \cdot B(OC_6H_5)_3$, 56237-27-5; $PtH(PEt_3)_2CN \cdot Al(CH_3)_3$, 56731-66-9; $PtH(PEt_3)_2CN \cdot Al(C_2H_5)_2(OC_2H_5)$, 60606-80-6; $[PtH(PEt_3)_2CN]_2NiCl_2$, 60594-97-0; $PtH(PEt_3)_2CN \cdot TiCl(C_5H_5)_2$, 56731-94-3; $PtH(PEt_3)_2CN$, 19528-87-1; $CoCl_2$, 7646-79-9; $ZnCl_2$, 7646-85-7; $NiCl_2$, 7718-54-9; $[(C_5H_5)_2TiCl]_2$, 1271-18-7; $HPt(PEt_3)_2Cl$, 16842-17-4.

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