technique was used to titrate freshly prepared aqueous solutions of sodium cobalt carbonylate. In this latter case, manometric analysis was also used.[10]

The coefficient of selectivity $K_{Co(CO)_4^-/I^-}$ defined in eq 4 was similarly obtained: into a two-phase system (10 mL of H_2O, 10 mL of CH_2Cl_2) at 20 °C were introduced 10 mmol of NaI, 0.1 mmol of $Bu_4N^+Br^-$, and 0.25 mmol of $NaCo(CO)_4$. After sufficient stirring, the amount of cobalt in the organic phase was determined as above and found to be 0.0053 M. Considering that all the introduced ammonium cation is present as a $Bu_4N^+Co(CO)_4^-$ or $Bu_4N^+I^-$ ion pair in the organic phase, due to the low aqueous solubility of these salts, $K_{Co(CO)_4^-/I^-}$ is directly available from formula 4. Selective analysis of the $Co(CO)_4^-$ anion in organic phase, during catalytic experiments, was made by IR analysis ($\nu_{C\equiv O}$ = 1900 cm^{-1}) after standardizing the IR spectrophotometer with a titrated solution of $Bu_4N^+Co(CO)_4^-$.

Quantitative Analysis of Products 6–11 (Table V). Phenylacetic acid (6): directly extracted, after acidification, from aqueous phase and weighted after evaporation of solvent.

Ester 7, ketone 8, and hydrocarbon 10: NMR ($\delta(CH_2)$) on the crude mixture resulting from evaporation of the organic phase, after destruction of any remaining cobalt carbonyl catalyst with iodine.

Toluene (9): GC analysis of the organic phase after introducing *p*-xylene as an internal standard.

Carbon dioxide (11): manometric measurement after prior destruction of the cobaltcarbonyl catalyst, followed by acidification of the aqueous phase with hydrochloric acid.

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Binuclear Isocyanide Complexes of Platinum(I). Facile N-Protonation and Alkylation of Bridging Isocyanide Ligands To Yield Bridging Aminocarbyne Complexes

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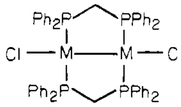
The platinum(I) dimers $Pt_2X_2(\mu\text{-dppm})_2$ (X = Cl, I) react with *p*-tolyl isocyanide (CNR) under various conditions to give $Pt_2X_2(\mu\text{-CNR})(\mu\text{-dppm})_2$, $[Pt_2X(CNR)(\mu\text{-dppm})_2]^+$, $[Pt_2(CNR)_2(\mu\text{-dppm})_2]^{2+}$, and $[Pt_2(\mu\text{-CNR})(CNR)_2(\mu\text{-dppm})_2]^{2+}$. The complexes with bridging isocyanides undergo facile N-protonation and alkylation to yield the series of complexes $[Pt_2L_2(\mu\text{-CNRR'})(\mu\text{-dppm})_2]^{n+}$ (L = X, R′ = H, Me, *n* = 1; L = CNR, R′ = H, Me, *n* = 3). All structural assignments are made on the basis of vibrational, ^1H NMR, and ^{31}P NMR spectroscopy.

Introduction

Over recent years, the chemistry of dinuclear complexes of Pd(I) and Pt(I), and the A-frame type complexes of Rh(I) and Ir(I), has been the subject of increasing attention. Much of the interest in this chemistry has focussed upon the ability of these complexes to coordinate small molecules (sometimes reversibly) and their ability to act as catalysts for certain processes[1,2] or serve as models for proposed intermediates in catalytic cycles.[3] The platinum(I) and palladium(I) bis(diphenylphosphino)methane (dppm) bridged dimers, $M_2Cl_2(\mu\text{-dppm})_2$, I, have an especially rich chemistry with regard to their ability to coordinate molecules via addition across the metal–metal bond, resulting in complexes of the type $[M_2Cl_2(\mu\text{-X})(\mu\text{-dppm})_2]^{n+}$, II. To date, examples with X = CO,[3,4] CNR,[4] CH_2,[3,4] H^+,[3] N_2R^+,[4] SO_2,[3,4] S,[3,4] Se,[5] C_2R_2,[3,4] and CS_2[6] have been isolated, although not necessarily with both metals. Unlike their rhodium analogues, however, these A-frame complexes of platinum and palladium have shown no tendency to coordinate small molecules or atoms to the face of the complex opposite the bridging ligand.



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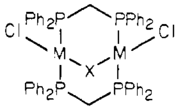

II

Our interest in the chemistry of such binuclear complexes centers principally upon the chemistry of the bridging ligand.[7] In particular, we are interested in the effect that binuclear activation can have upon the chemistry of the bridging group itself and also in the effect that varying the bridghead ligand has upon the chemistry of the complex as a whole. The complex $Pt_2Cl_2(\mu\text{-dppm})_2$ appears as an ideal starting point for investigating the chemistry of the bridging groups in dinuclear complexes for two reasons: (i) the great reactivity of the Pt–Pt bond gives access to a wide variety of bridging groups and (ii) investigating the chemistry of the bridging group is not hampered by competing reactions occurring on the other face of the dimer. When this project was initiated, dimeric,

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dppm-bridged isocyanide complexes of platinum were unknown, despite the fact that $Pt_2Cl_2(\mu\text{-dppm})_2$ was known to react with CO[8] and that the analogous palladium system exhibited an extensive chemistry.[9] This paper deals with elaboration of the $Pt_2X_2(\mu\text{-dppm})_2$ (X = Cl, I)/*p*-tolyl isocyanide (CNR) system in which both terminal and bridging isocyanide complexes occur. In the case of the bridging isocyanide complexes, facile N-protonation and alkylation takes place to give complexes that can be formally regarded as having bridging carbyne ligands.

Experimental Section

Physical Measurements. Infrared spectra were recorded on Perkin-Elmer 180 or 283B grating spectrophotometers as either Nujol mulls on KBr plates or CH_2Cl_2 solutions in NaCl cells. Calibration was achieved with either polystyrene or indene. ^1H NMR spectra were recorded on a Varian Associates CFT20 spectrometer using Me_4Si as internal calibrant. ^{31}P NMR spectra were obtained on a Varian Associates XL100 spectrometer of the National Research Council Atlantic Regional Laboratory, whose assistance is gratefully acknowledged. Samples were run as CD_2Cl_2 solutions in 5-mm tubes, and chemical shifts were determined relative to 85% phosphoric acid as an external standard. Melting points were obtained with a Fisher-Johns apparatus and are uncorrected. Elemental analyses were performed by Guelph Chemical Laboratories Ltd., Ontario, and the Canadian Microanalytical Service Ltd., British Columbia. Conductivity measurements were performed at 25 °C on ca. 10^{-3} M solutions in either acetone, nitromethane, or dichloromethane, using an Industrial Instruments conductivity bridge. The cell constant was determined by using 0.0100 M KCl solution.

Materials. $Pt_2Cl_2(\mu\text{-dppm})_2$ and $Pt_2I_2(\mu\text{-dppm})_2$ were prepared by using previously published procedures.[10] *p*-Tolyl isocyanide was prepared by the dehydration of *p*-tolylformamide using a standard procedure.[11] The isocyanide was handled by preparing a 10.0-mg mL^{-1} solution in dichloromethane, which was stored at −18 °C and used in all preparations. All solvents were appropriately dried and distilled before being stored over Linde type 4A molecular sieves. All preparative procedures were performed under an atmosphere of prepurified nitrogen. Although all complexes were found to be air stable in both the solid state and solution, some were hygroscopic. All complexes prepared were subject to vacuum drying at 100 °C prior to the recording of analytical and physical data, unless specified otherwise.

Preparation of Complexes. $Pt_2Cl_2(\mu\text{-CNR})(\mu\text{-dppm})_2$ (1). To a solution of $Pt_2Cl_2(\mu\text{-dppm})_2$ (0.50 g, 0.41 mmol) in 30 mL of dichloromethane was added *p*-tolyl isocyanide solution (4.8 mL, 0.41 mmol) dropwise. To the now golden yellow solution was added 30 mL of benzene, and the solution was left stirring until crystallization began (ca. 1 h). The dichloromethane was removed slowly under reduced pressure and the orange-yellow product removed by filtration and washed with hexane. A more crystalline material could sometimes be obtained by immediately removing most of the dichloromethane and allowing the resultant solution to stand undisturbed for an extended period of time. The material obtained in this fashion was sufficiently pure for most purposes although small samples of the sparingly soluble material could be recrystallized from dichloromethane–benzene: yield 0.45 g (82%); mp 286–288 °C. Anal. Calcd for $C_{58}H_{51}NP_4Cl_2Pt_2$: C, 51.71; H, 3.82; N, 1.04; P, 9.20. Found: C, 51.70; H, 3.88; N, 1.11; P, 9.45.

$Pt_2I_2(\mu\text{-CNR})(\mu\text{-dppm})_2$ (2). To a solution of $Pt_2I_2(\mu\text{-dppm})_2$ (0.20 g, 0.14 mmol) in 15 mL of dichloromethane was added *p*-tolyl isocyanide solution (1.7 mL, 0.14 mmol). To the resultant orange solution was added diethyl ether until precipitation commenced. The solution was then set aside until crystallization was complete, and the orange crystals of the product were removed by filtration and recrystallized from dichloromethane–diethyl ether: yield 0.21 g (97%); mp 196–204 °C with RNC elimination. Anal. Calcd for $C_{58}H_{51}NI_2P_4Pt_2$: C, 45.53; H, 3.36; N, 0.91; I, 16.59. Found: C, 46.56; H, 3.55; N, 1.01; I, 17.27.

$[Pt_2Cl(CNR)(\mu\text{-dppm})_2]PF_6$ (3). To $Pt_2Cl_2(\mu\text{-dppm})_2$ (0.20 g, 0.16 mmol) dissolved in 20 mL of dichloromethane was added 1.9 mL of *p*-tolyl isocyanide solution (0.019 g, 0.16 mmol) dropwise. To the resultant golden yellow solution was added a filtered solution of $NaPF_6$ (0.10 g, 0.59 mmol) in ethanol (20 mL). The faint precipitate of NaCl formed was removed by filtering the solution through a pad of Celite and the filtrate concentrated to ca. 5 mL. On standing, well-formed yellow needles of the product separated. Recrystallization was from dichloromethane–ethanol: yield 0.20 g (84%); mp 276–278 °C. Anal. Calcd for $C_{58}H_{51}NP_5ClF_6Pt_2$: C, 47.83; H, 3.53; N, 0.96; P, 10.63. Found: C, 47.37; H, 3.85; N, 0.97; P, 11.19.

$[Pt_2I(CNR)(\mu\text{-dppm})_2]PF_6$ (4). To a solution of $Pt_2I_2(\mu\text{-dppm})_2$ (0.20 g, 0.14 mmol) in 30 mL of dichloromethane was added 1.7 mL of *p*-tolyl isocyanide solution (0.017 g, 0.14 mmol) followed by 10 mL of ethanol and a filtered solution of $NaPF_6$ (0.20 g, 1.2 mmol) in 20 mL of ethanol. The resultant bright yellow solution was evaporated slowly under reduced pressure, and the crystals were collected by filtration before being washed with ethanol and hexane. Recrystallization from dichloromethane–ethanol gave the product as fine, bright yellow needles: yield 0.19 g (87%); mp 198–202 °C. Anal. Calcd for $C_{58}H_{51}NP_5IF_6Pt_2$: C, 45.00; H, 3.32; N, 0.90; P, 10.00. Found: C, 44.96; H, 3.23; N, 1.03; P, 10.15.

$[Pt_2(CNR)_2(\mu\text{-dppm})_2](ClO_4)_2$ (5). $Pt_2Cl_2(\mu\text{-dppm})_2$ (0.50 g, 0.41 mmol) was suspended in 30 mL of methanol in which $NaClO_4$ (0.50 g, 4.1 mmol) had been dissolved. A total of 9.6 mL of *p*-tolyl isocyanide solution (0.096 g, 0.82 mmol) was added in a number of small aliquots (ca. 0.2–0.5 mL). After the addition of each aliquot, the solution turned orange and was allowed to stir until colorless. When the addition was complete, an almost colorless solution resulted, which was filtered to remove NaCl and some unreacted $Pt_2Cl_2(\mu\text{-dppm})_2$. If at the end of the addition the solution remained orange, some excess $Pt_2Cl_2(\mu\text{-dppm})_2$ was added until the color was discharged. The filtered solution was evaporated to dryness, extracted with ca. 30 mL of dichloromethane, and filtered to remove excess $NaClO_4$. Upon the addition of 30–40 mL of ethanol and evaporation under reduced pressure, the product deposited in the form of heavy cream crystals. Recrystallization was from dichloromethane–ethanol: yield 0.58 g (90%, based on $Pt_2Cl_2(\mu\text{-dppm})_2$ at start); mp 281–283 °C dec. Anal. Calcd for $C_{66}H_{58}N_2P_4Cl_2O_8Pt_2$: C, 49.79; H, 3.67; N, 1.76; P, 7.78. Found: C, 49.56; H, 3.90; N, 1.68; P, 8.08.

$[Pt_2(\mu\text{-CNR})(CNR)_2(\mu\text{-dppm})_2](ClO_4)_2$ (6). To $Pt_2Cl_2(\mu\text{-dppm})_2$ (0.25 g, 0.20 mmol) was added a solution of $NaClO_4$ (0.15 g, 1.2 mmol) in methanol (20 mL) followed by 9.5 mL of *p*-tolyl isocyanide solution (0.095 g, 0.81 mmol). The resultant suspension was stirred until all the starting material was in solution, filtered to remove NaCl, and evaporated to dryness. The resultant orange residue was extracted with 20 mL of dichloromethane and filtered to remove excess $NaClO_4$, and 30 mL of ethanol was added. When this solution was evaporated to ca. 10 mL, well-formed bright orange crystals of the product separated. Recrystallization was from dichloromethane–ethanol with several drops of added *p*-tolyl isocyanide solution: yield 0.30 g (85%); mp 210–215 °C with isocyanide evolution. Anal. Calcd for $C_{74}H_{65}N_3P_4Cl_2O_8Pt_2$: C, 52.00; H, 3.83; N, 2.46; P, 7.25. Found: C, 51.88; H, 3.99; N, 2.36; P, 7.76.

$[Pt_2Cl_2(\mu\text{-CN[H]R})(\mu\text{-dppm})_2]ClO_4$ (7). To $Pt_2Cl_2(\mu\text{-CNR})(\mu\text{-dppm})_2$ (0.15 g, 0.11 mmol) suspended in 15 mL of CH_2Cl_2 was added 10 mL of ethanol and 0.1 mL of 70% $HClO_4$. The mixture was stirred briefly until solution of the starting material was effected, resulting in a color change from golden yellow to colorless. On evaporation under reduced pressure, cream crystals of the product separated that were removed by filtration and washed with ethanol acidified with 70% $HClO_4$ (1 drop in ca. 30 mL) and with hexane. Recrystallization was from dichloromethane–acidified ethanol: yield 0.12 g (75%); mp 227–229 °C. Anal. Calcd for $C_{58}H_{52}NP_4Cl_3O_4Pt_2$: C, 48.13; H, 3.62; N, 0.97; P, 8.56. Found: C, 47.42; H, 3.50; N, 0.93; P, 8.06.

$[Pt_2Cl_2(\mu\text{-CN[Me]R})(\mu\text{-dppm})_2]I$ (8). To $Pt_2Cl_2(\mu\text{-CNR})(\mu\text{-dppm})_2$ (0.15 g, 0.11 mmol) suspended in 15 mL of dichloro-

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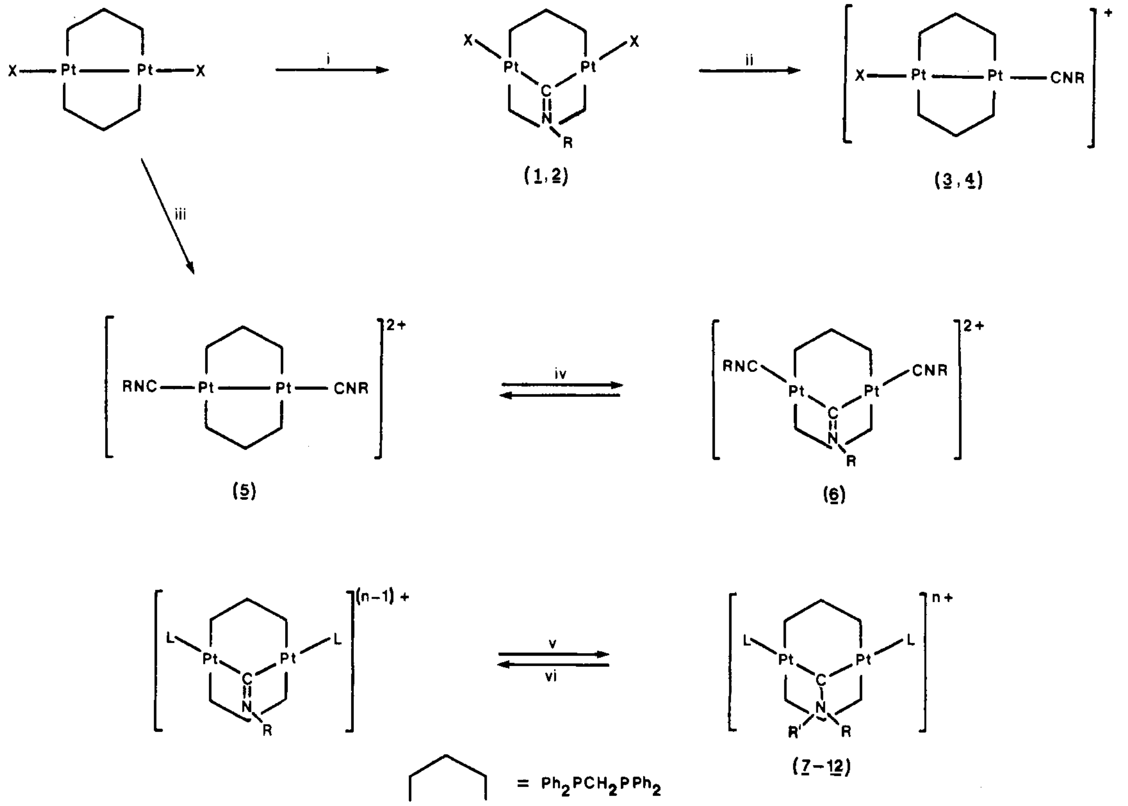
Scheme I



(i) 1 equiv of RNC in CH_2Cl_2; (ii) EtOH, $NaPF_6$; (iii) 2 equiv of RNC in MeOH; (iv) excess RNC; (v) $HClO_4$, R' = H, L = X, *n* = 1; L = CNR, *n* = 3; MeI, R' = Me; L = X, *n* = 1; L = CNR, *n* = 3; (vi) NEt_3, R' = H.

methane was added 2 mL of CH_3I. The mixture was stirred until the reaction was complete, as evidenced by a change in color from golden yellow to off-white. The product was precipitated by the addition of ca. 30 mL of diethyl ether and removed by filtration. Recrystallization was from dichloromethane–ethanol: yield 0.15 g (90%); mp >300 °C dec. Anal. Calcd for $C_{59}H_{54}NP_4Cl_2IPt_2$: C, 47.59; H, 3.66; N, 0.94; Cl, 4.76; I, 8.53. Found: C, 46.57; H, 3.63; N, 0.96; Cl, 4.60; I. 7.23.

$[Pt_2I_2(\mu\text{-}CN[H]R)(\mu\text{-}dppm)_2]ClO_4$ (9). A procedure similar to that employed for compound 7 above but using $Pt_2I_2(\mu\text{-}CNR)(\mu\text{-}dppm)_2$ (0.15 g, 0.10 mmol) yielded the product as pale yellow crystals. The crystals were removed by filtration, washed with acidified ethanol and hexane, and recrystallized from dichloromethane–acidified ethanol: yield 0.14 g (80%); mp 233–234 °C. Anal. Calcd for $C_{58}H_{52}NI_2P_4ClO_4Pt_2$: C, 42.73; H, 3.22; N, 0.86; I, 15.57. Found: C, 42.41; H, 3.30; N, 1.00; I, 12.73.

$[Pt_2I_2(\mu\text{-}CN[Me]R)(\mu\text{-}dppm)_2]I$ (10). A procedure similar to that employed for compound 8 above but using $Pt_2I_2(\mu\text{-}CNR)(\mu\text{-}dppm)_2$ (0.15 g, 0.10 mmol) yielded the product as a yellow powder that was recrystallized from dichloromethane–ethanol: yield 0.16 g (95%); mp >200 °C dec. Anal. Calcd for $C_{59}H_{54}NI_3P_4Pt_2$: C, 42.38; H, 3.26; N, 0.84; I, 22.77. Found: C, 42.64; H, 3.54; N, 0.74; I, 20.25.

$[Pt_2(\mu\text{-}CN[H]R)(CNR)_2(\mu\text{-}dppm)_2](ClO_4)_3$ (11). To a solution of $[Pt_2(\mu\text{-}CNR)(CNR)_2(\mu\text{-}dppm)_2](ClO_4)_2$ (0.10 g, 0.059 mmol) in 20 mL of dichloromethane–ethanol (1:1 v/v) was added sufficient 70% $HClO_4$ to discharge completely the orange color of the starting material. On the removal of the dichloromethane from the colorless solution, the product precipitated from solution as a mass of fine white needles. After filtration and washing with acidified ethanol, the product was recrystallized from dichloromethane–acidified ethanol, filtered, and washed with diethyl ether: yield 0.10 g (94%); mp 194–196 °C dec. Anal. Calcd for $C_{74}H_{66}N_3P_4Cl_3O_{12}Pt_2$: C, 49.11; H, 3.68; N, 2.32. Found: C, 48.59; H, 3.47; N, 2.27.

$[Pt_2(\mu\text{-}CN[Me]R)(CNR)_2(\mu\text{-}dppm)_2](ClO_4)_3$ (12). To a solution of $[Pt_2(\mu\text{-}CNR)(CNR)_2(\mu\text{-}dppm)_2](ClO_4)_2$ (0.20 g, 0.12 mmol) in 15 mL of dichloromethane was added 2 mL of CH_3I. The resultant orange-red solution was heated under reflux for 24 h after which time the color had turned to pale yellow. After the addition of $NaClO_4$ (0.20 g, 1.6 mmol) in 20 mL of ethanol, evaporation under reduced pressure resulted in the formation of pale yellow crystals of the product. Recrystallization was from dichloromethane–ethanol: yield 0.18 g (83%); mp 291–292 °C dec. Anal. Calcd for $C_{75}H_{68}N_3P_4Cl_3O_{12}Pt_2$: C, 49.38; H, 3.76; N, 2.30. Found: C, 48.47; H, 3.62; N, 2.16.

Results and Discussion

Reactions of $Pt_2X_2(\mu\text{-}dppm)_2$ (X = Cl, I) with *p*-Tolyl Isocyanide. In dichloromethane solution, $Pt_2Cl_2(\mu\text{-}dppm)_2$ reacts with 1 equiv of *p*-tolyl isocyanide (CNR) to form a golden yellow solution. Adding benzene to such solutions precipitates the product $Pt_2Cl_2(\mu\text{-}CNR)(\mu\text{-}dppm)_2$ (1, Scheme I) which is only sparingly soluble when in a crystalline form. On occasions, a more soluble, amorphous form of 1 coprecipitates which can be removed (if desired) by washing with dichloromethane. The corresponding reaction employing $Pt_2I_2(\mu\text{-}dppm)_2$ as substrate proceeds in the same manner to yield orange $Pt_2I_2(\mu\text{-}CNR)(\mu\text{-}dppm)_2$ (2). This complex, however, is more prone to oiling when isolated in this fashion, whereas the use of diethyl ether as a precipitating agent results in an excellent isolated yield of crystalline 2. The tendency of 1 and 2 to form oils is probably related to their remarkably hygroscopic nature. Infrared spectra of freshly prepared 1 and 2 show medium intensity absorptions at ca. 3600 and 1620 cm^{-1} that can be attributed to the stretching and bending vibrations of water. On rigorous drying under vacuum, these absorptions disappear completely but on standing in the open, the dry samples slowly rehydrate. In view of the basicity of the nitrogen atom in these bridging isocyanide complexes (vide infra), it seems most likely that the absorbed water is hydrogen bound to the nitrogen atom. The occurrence of a band at 1620 cm^{-1} is particularly noteworthy, since a band in this region has been reported by Benner and Balch[9] to occur in various dipalladium complexes also containing bridging isocyanides. It seems reasonable, therefore, to infer that bound water is the origin of the extra band in the palladium complexes. The infrared spectra of **1** and **2** (Table I) exhibit ν(C=N) of the bridging isocyanide groups at characteristically low values of 1531 and 1523 cm^{-1}, indicating that the isocyanide can best be regarded as a dimetalated imine, analogous to $Pt_2Cl_2(\mu\text{-}CO)(\mu\text{-dppm})_2$ in which the carbonyl group has been likened to a dimetalated ketone.[12] The insolubility of **1** and **2** rendered the recording of ^{1}H NMR spectra very difficult. A reasonable spectrum of **1** (Table II) can be obtained, however, by precipitating the complex as an oil, dissolving the oil in $CDCl_3$, and running the spectrum quickly before crystallization occurs. The presence of the isocyanide is confirmed by a singlet at 1.98 ppm and an AB quartet centered at ca. 6.6 ppm. The methylene protons give rise to an unresolved multiplet centered at 3.13 ppm.

Like their palladium analogues,[9] **1** and **2** show no tendency to dissociate isocyanide. In polar media, however, **1** and **2** isomerize to give the yellow cations $[Pt_2X(CNR)(\mu\text{-dppm})_2]^+$ (**3**, X = Cl; **4**, X = I) which can be isolated as their PF_6^- (or ClO_4^-) salts. Thus when ethanol is added to an orange-yellow solution of **1** in dichloromethane, formed either in situ or by dissolution of **1**, a color change to pale yellow occurs and the addition of $NaPF_6$ dissolved in ethanol eventually yields **3**. This behavior is entirely analogous to that observed for $Pt_2Cl_2(\mu\text{-}CO)(\mu\text{-dppm})_2$,[8] although we have not observed any substantial evidence to suggest that the isomerization of either **1** to **3** or **2** to **4** is reversible. Surprisingly, the palladium analogues of **3** and **4** have not been observed, although the conductivities of $Pd_2X_2(\mu\text{-CNMe})(\mu\text{-dppm})_2$ are reported to be unusually high in acetonitrile solution.[9] The spectroscopic properties of **3** and **4** are fully in accord with their proposed structures. In the infrared spectra, only terminal ν(CN) absorptions are observed and the absorptions associated with bridging ν(C=N) and bound water are no longer present. The ^{1}H NMR spectra of both **3** and **4** are essentially the same as that of $[Pt_2Cl(CO)(\mu\text{-dppm})_2]PF_6$ with respect to the dppm methylene protons.[8] With the more soluble **3**, the $-CH_2-$ multiplet appears as a triplet of triplets, although both triplet sets have the appearance of being the inner three lines of quintets. The triplet due to $^1H-^{195}Pt$ coupling (^3J(PtH) = 59 Hz) has approximately the 8:18:8 intensity ratio required by the structure assignment, and the triplets due to $^1H-^{31}P$ coupling (^2J(PH) = 3.5 Hz) have an approximately 1:1.5:1 intensity ratio, suggesting that the methylene protons are coupled to two pairs of virtually coupled phosphorus atoms, with approximately equal coupling constants of 3.5 Hz. The lower solubility of **4** prevented the observation of $^1H-^{31}P$ coupling, although $^1H-^{195}Pt$ coupling could still be observed. In order to avoid interference from the PF_6^- ion in the ^{31}P NMR spectra of **3** and **4**, the ClO_4^- salts were prepared either by direct methods or by recrystallizing the PF_6^- salts repeatedly in the presence of an excess of $NaClO_4$ until all traces of PF_6^- were removed (infrared). Unfortunately, only the perchlorate salt of **4** was sufficiently soluble to allow a spectrum to be obtained. The observed spectrum of **4** can be successfully interpreted as a combination of AA′BB′, AA′BB′X, and AA′BB′Y subspectra as has been previously described.[8] The derived coupling constants (Table III) are comparable in magnitude to those reported for $[Pt_2Cl(CO)(\mu\text{-dppm})_2]^+$, al-

Table I. Infrared and Conductivity Data

compound	ν(CN)[a]	ν(C=N)[b]	others	Λ_m[c] CH$_3$COCH$_3$	Λ_m[c] CH$_3$NO$_2$	Λ_m[c] CH$_2$Cl$_2$
1, $Pt_2Cl_2(\mu\text{-CNR})(\mu\text{-dppm})_2$		1531 (m)	ν(PtCl) 237 (s, br)			
2, $Pt_2I_2(\mu\text{-CNR})(\mu\text{-dppm})_2$		1523 (m)				
3, $[Pt_2Cl(CNR)(\mu\text{-dppm})_2]PF_6$	2169 (vs)		ν(PtCl) 266 (s)	140.0	insol	
4, $[Pt_2I(CNR)(\mu\text{-dppm})_2]PF_6$	2170 (vs)			133.7	82.7	45.8
5, $[Pt_2(CNR)_2(\mu\text{-dppm})_2](ClO_4)_2$	2180 (sh), 2168 (vs)			233.4	177.0	
6, $[Pt_2(\mu\text{-CNR})(CNR)_2(\mu\text{-dppm})_2](ClO_4)_2$	2178 (s)	1583 (w), 1567 (w)		215.1		
7, $[Pt_2Cl_2(\mu\text{-CN[H]R})(\mu\text{-dppm})_2]ClO_4$		1509 (sh), 1504 (m)	δ(NH) 1525 (w, br) ν(PtCl) 280 (s, br)	149.1		24.0
8, $[Pt_2Cl_2(\mu\text{-CN[Me]R})(\mu\text{-dppm})_2]I$		1506 (m)	ν(PtCl) 283, 270 (s, br)	insol	insol	35.4
9, $[Pt_2I_2(\mu\text{-CN[H]R})(\mu\text{-dppm})_2]ClO_4$		1503 (sh), 1499 (m)	δ(NH) 1532 (w, br)	142.2		21.2
10, $[Pt_2I_2(\mu\text{-CN[Me]R})(\mu\text{-dppm})_2]I$		1506 (m)		insol	insol	34.5
11, $[Pt_2(CNR)_2(\mu\text{-CN[H]R})(\mu\text{-dppm})_2](ClO_4)_3$	2201 (s)	1540 (w)	δ(NH) see text	276.7		34.4
12, $[Pt_2(CNR)_2(\mu\text{-CN[Me]R})(\mu\text{-dppm})_2](ClO_4)_3$	2201 (s)	1532 (w)		202.8	232.0	15.6

[a] CH_2Cl_2 solution. [b] Kel-F mull. [c] In cm^2 Ω^{-1} equiv^{-1}.

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(12) Brown, M. P.; Keith, A. N.; Manojlović-Muir, Lj.; Muir, K. W.; Puddephatt, R. J.; Seddon, K. R. *Inorg. Chim. Acta* **1979**, *34*, L223.

Table II. ^{1}H NMR Data[a]

compound	$\delta(^1\text{H})^b$ tol-CH$_3$	-CH$_2$-	others[c]
1, $Pt_2Cl_2(\mu\text{-CNR})(\mu\text{-dppm})_2$	1.98 (s)	3.13 (m)	ca. 6.6 (q, C_6H_4)
3, $[Pt_2Cl(CNR)(\mu\text{-dppm})_2]PF_6$	2.18 (s)	4.56 (m, ^3J(PtH) = 59, ^2J(PH) = 3.5)	6.41 (q, C_6H_4)
4, $[Pt_2I(CNR)(\mu\text{-dppm})_2]PF_6$	2.19 (s)	4.69 (m, ^3J(PtH) = 65)	6.44 (q, C_6H_4)
5, $[Pt_2(CNR)_2(\mu\text{-dppm})_2(ClO_4)_2$	2.19 (s)	5.29 (m, ^3J(PtH) = 56, ^2J(PH) = 4.4)	6.50 (q, C_6H_4)
6, $[Pt_2(\mu\text{-CNR})(CNR)_2(\mu\text{-dppm})_2](ClO_4)_2$	2.26 (s)	(3.1, 6.3)[d]	6.94 (q, C_6H_4)
7, $[Pt_2Cl_2(\mu\text{-CN[H]R})(\mu\text{-dppm})_2]ClO_4$	2.03 (s)	(3.2)[d]	
8, $[Pt_2Cl_2(\mu\text{-CN[Me]R})(\mu\text{-dppm})_2]I$	1.92 (s)	(3.5)[d]	3.48 (s, NCH_3)
9, $[Pt_2I_2(\mu\text{-CN[H]R})(\mu\text{-dppm})_2]ClO_4$	2.13	(3.2)[d]	
10, $[Pt_2I_2(\mu\text{-CN[Me]R})(\mu\text{-dppm})_2]I$	1.99	(3.4)[d]	3.83 (s, NCH_3)

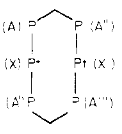
[a] In $CDCl_3$ solution. [b] Coupling constants in hertz. [c] All complexes exhibit phenyl proton resonances at ca. 7.2–7.4 ppm. [d] See text.

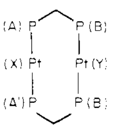
Table III. ^{31}P NMR Data

complex	$\delta(^{31}\text{P})$	coupling constants[a] J(AX)	J(AX′)	J(AA″)	J(AA‴)	N′ (calcd)
5, $[Pt_2(CNR)_2(\mu\text{-dppm})_2](ClO_4)_2$	−4.62	2561.5	−92.1	51.8	31.4	2469.4 (2469.4)
6, $[Pt_2(\mu\text{-CNR})(CNR)_2(\mu\text{-dppm})_2](ClO_4)_2$	15.70	3250	230	49	~0	3490 (3480)

complex	$\delta(^{31}\text{P})$	coupling constants[a] J(AX)	J(BY)	$\lvert J(\text{AY})\rvert^b$	$\lvert J(\text{BX})\rvert^b$	J(AB)	J(AB′)
4, $[Pt_2I(CNR)(\mu\text{-dppm})_2]ClO_4$	−1.58, −6.90	2612	2779	124	90	57.2	29.8
10, $[Pt_2I_2(\mu\text{-CN[Me]R})(\mu\text{-dppm})_2]I$	−2.50, −3.90	2935	3060	129	132	30.7	0.8
8, $[Pt_2Cl_2(\mu\text{-CN[Me]R})(\mu\text{-dppm})_2]I$	1.98, 1.00	3015	3120	134	140	36.5[c]	1.2[c]

[a] Hertz. See diagram for notation:





[b] See text. [c] Tentative only. See text.

though certain minor differences occur. The most significant value is that of 29.8 Hz for J(AB′) which is in the range normally associated with dimers containing a strong Pt–Pt bond.[13] The presence of a Pt–Pt bond also makes it highly likely that both J(AY) and J(BX) are negative, despite the fact that their sign cannot be determined directly. The ^{31}P NMR spectra of both **4** and **10** (vide infra) have been successfully simulated by using the parameters listed.[14]

Reacting $Pt_2X_2(\mu\text{-dppm})_2$ with 2 equiv of RNC in dichloromethane solution yields as yet uncharacterized materials containing both terminal and bridging isocyanide groups. These products are obviously very closely related to such palladium complexes as $[Pd_2X(MeNC)(\mu\text{-MeNC})(\mu\text{-dppm})_2]X$,[9] but certain of their physical and spectroscopic properties cannot at present be rationalized. Nevertheless, when $Pt_2Cl_2(\mu\text{-dppm})_2$ is reacted with 2 equiv of RNC in methanol suspension, an almost colorless solution results from which can be isolated salts of the cation $[Pt_2(CNR)_2(\mu\text{-dppm})_2]^{2+}$ (**5**). Infrared, ^{1}H NMR, and ^{31}P NMR spectra all confirm the assigned structure. In the ^{1}H NMR, the methylene protons give rise to an apparent triplet of triplets (^3J(PtH) = 56 Hz, ^2J(PH) = 4.4 Hz) with the two outer signals of the expected 1:8:18:8:1 quintet due to Pt–H coupling being barely discernible. The ^{31}P NMR spectrum indicates an equivalent environment for all four phosphorus atoms, and analysis of the AA′A″A‴X and AA′A″A‴XX′ subspectra gives the derived coupling constants in Table III.[10] Not surprisingly, the values of J(AX′), J(AA″), and J(AA‴) for **5** are closely comparable to those of $[Pt_2(CO)_2(\mu\text{-dppm})_2]^{2+}$, which has been assigned a similar structure.[13] The infrared spectrum of **5** in the terminal ν(CN) region is unusual in that the observed band is distinctly asymmetric. In the solid state, this asymmetry often manifests itself as a well-resolved doublet. Although not reported for the carbonyl analogue of **5**, $[Pt_2(CO)_2(\mu\text{-dppm})_2]^{2+}$, the apparent nonlinearity of the RNC–Pt–Pt–CNR fragment of **5** does have precedent in the structure of $[Pt_2Cl(CO)(\mu\text{-dppm})_2]^+$, in which the Cl–Pt–Pt and Pt–Pt–C bond angles are 178.3 (1)° and 171.3 (8)°, respectively.[15]

Reacting a colorless solution of **5** with excess isocyanide yields a red-orange solution from which crystals of $[Pt_2(\mu\text{-CNR})(CNR)_2(\mu\text{-dppm})_2](ClO_4)_2$ (**6**) can be isolated. Spectroscopically, **6** is very similar to its palladium analogue.[9] In the infrared spectrum, the terminal isocyanide groups give rise to a single, very strong absorption at 2178 cm^{-1} (CH_2Cl_2), and in the solid state the bridging isocyanide group gives rise to two absorptions at 1583 and 1567 cm^{-1}. Both ^{1}H and ^{31}P NMR spectra of **6** show the

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(13) Brown, M. P.; Fisher, J. R.; Franklin, S. J.; Puddephatt, R. J.; Seddon, K. R. *J. Organomet. Chem.* **1978**, *161*, C46.

(14) Seddon, K. R., personal communication.

(15) Manojlović-Muir, Lj.; Muir, K. W.; Solomun, T. *J. Organomet. Chem.* **1979**, *179*, 479.

complex to be fluxional at the probe temperature of 25 °C. In the ^{1}H NMR, the tolyl methyl protons occur as a singlet and only one AB quartet for the *p*-phenyl protons is observed, indicating an equivalent environment for all three isocyanide groups. Adding free RNC to the solution results only in a shift of the methyl signal from 2.26 to 2.36 ppm, suggesting that both inter- and intramolecular processes contribute to the fluxional nature of **6**. The resonance belonging to the methylene protons could not be identified unambiguously. Two similarly shaped, broad, and unresolved peaks occur at ca. 3.1 and 6.3 ppm, irrespective of the history of the sample. In view of the trend seen in compounds **1**–**5** in which the methylene multiplets occur to lower field as the charge on the complex increases, it seems that the signal at 6.3 ppm is most likely due to the methylene protons. The origin of the peak at 3.1 ppm still remains unexplained. The ^{31}P NMR spectrum of **6** is similar to that of **5** although the lines are considerably more broad and less well resolved. The pattern of the AA′A″A‴X subspectrum, however, is typical of such species as $Pt_2Cl_2(\mu\text{-}CH_2)(\mu\text{-dppm})_2$[16] in which $J(AA''') \simeq 0$ as a result of the lack of a Pt–Pt bond. The AA′A″A‴XX′ subspectrum indicates that both $J(AX')$ and $J(AX)$ are of the same sign (presumably positive) which has also been construed as indicative of the absence of a Pt–Pt bond.[13] The observation of exchange between free and coordinated RNC in solutions of **6** suggests that RNC dissociation may take place, unlike most other complexes with bridging isocyanides. This hypothesis was confirmed by noting that solutions of **6** very slowly (several days) lost RNC to yield **5**. In the solid state, however, this process is essentially halted (no significant change after 2 months at 60 °C) despite the fact that crystals of **6** always smell faintly of isocyanide.

The ionic nature of compounds **3**–**6** was established by conductivity measurements (Table I). The conductivity of **4** in all three solvents was evaluated to serve as a reference 1:1 electrolyte.

Electrophilic Attack at the Bridging Isocyanide Groups in 1, 2, and 6. The hygroscopic nature of **1** and **2** and the observation that both bent terminal[17] and bridging[18] isocyanides can be alkylated and protonated suggested to us that the bridging isocyanide groups in **1**, **2**, and **6** might be subject to electrophilic attack. Accordingly, the reactions of these three compounds with H^+ and CH_3I were investigated. Compound **1** reacts rapidly with $HClO_4$ in CH_2Cl_2/ethanol suspension to give a colorless solution from which fine crystals of $[Pt_2Cl_2(\mu\text{-CN}[H]R)(\mu\text{-dppm})_2]ClO_4$ (**7**) can be isolated. Washing solid **7** with ethanol causes the white to cream solid to change to varying shades of yellow. Similarly, if ethanol is added to a dichloromethane solution of **7**, a color change to yellow is observed. If, however, the above procedures are performed with ethanol to which a trace of $HClO_4$ has been added, no color changes are observed. It seems reasonable, therefore, to attribute these color changes to the partial deprotonation of **7** brought about by polar media. In fact, **7** can be completely deprotonated to **1** in dichloromethane by the addition of an equivalent amount of NEt_3. Compound **2** also reacts with $HClO_4$ under similar conditions to yield $[Pt_2I_2(\mu\text{-CN}[H]R)(\mu\text{-dppm})_2]ClO_4$ (**9**). The reactions of **1** and **2** with CH_3I, however, differ. $Pt_2I_2(\mu\text{-CNR})(\mu\text{-dppm})_2$ reacts with CH_3I to give yellow $[Pt_2I_2(\mu\text{-CN}[Me]R)(\mu\text{-dppm})_2]I$ (**10**) cleanly and in good yield. $Pt_2Cl_2(\mu\text{-CNR})(\mu\text{-dppm})_2$, on the other hand, reacts with CH_3I to give a product ranging in color from almost colorless to yellow. The ^{31}P NMR spectra (vide infra) of these materials indicate that a mixture of $[Pt_2Cl_2(\mu\text{-CN}[Me]R)(\mu\text{-dppm})_2]I$ (**8**) and the cation of compound **10** is being formed. Pale yellow mixtures containing predominantly or exclusively **8** are the most common, but it is not unusual to be able to isolate salts of **10** from this reaction, contaminated with only a small proportion of **8**. Adventitious free radicals are presumably responsible for the exchange of halogen between CH_3I and PtCl groups, although we have not performed any experiments to verify that hypothesis. In view of the expectation that extensive scrambling would occur between the two halide environments of **8**,[19] it is perhaps surprising that only one coordination isomer is formed. Despite the dipositive charge on **6**, it also reacted with $HClO_4$ and CH_3I. Not surprisingly, the reaction of **6** with CH_3I was much slower than that between **1** and **2** and CH_3I. The protonated and alkylated products of **6**, $[Pt(CNR)_2(\mu\text{-CN}[H]R)(\mu\text{-dppm})_2](ClO_4)_3$ (**11**), and $[Pt_2(CNR)_2(\mu\text{-CN}[Me]R)(\mu\text{-dppm})_2](ClO_4)_3$ (**12**), are very hygroscopic, and because of their similarity to the products described above, their characterization was limited to elemental analysis and infrared spectroscopy.

The infrared spectra of compounds **7**–**12** all show similar features in the 1500–1600 cm^{-1} region. For compounds **7** to **10**, ν(C=N) of the modified isocyanide could not be assigned unambiguously because of the occurrence of a band at ca. 1505 cm^{-1} arising from the *p*-tolyl group. In all probability, however, the more intense of the two bands (seen in **7** and **9**) can be attributed to ν(C=N). In compounds **11** and **12**, ν(C=N) occurs at a somewhat higher value, and, in the case of **11**, it appears that both ν(C=N) (sharp) and δ(NH) (broad) overlap. The solubility of compounds **7**–**10** in $CDCl_3$ is rather low which made it difficult to assign resonances attributable to the methylene protons and, where applicable, the NH protons. In general however, weak absorptions around 3.0–3.5 ppm were observed, presumably arising from the methylene protons. The methyl resonances were easily identified but rather uninformative. Of the compounds **7**–**10**, only **8** and **10** proved sufficiently soluble for ^{31}P NMR studies. The spectrum obtained for **10**, the more soluble of the two, is consistent with the geometry assigned and indicates that there is restricted rotation about the C–N bond, since two different environments exist for the phosphorus atoms. Analysis of the AA′BB′ pattern and the principal AA′BB′X and AA′BB′Y subspectra can be performed readily and the coupling constants in Table III assigned. The most notable difference between the spectra of **4** and **10** is manifested in the values of $J(AB') = 29.8$ and 0.8 Hz, respectively. As mentioned earlier, a value as low as that exhibited by **10** is indicative of no Pt–Pt interaction, which in turn implies that both $J(AY)$ and $J(BX)$ are likely to be positive.[13] The principal subspectra of compound **8** could also be analyzed easily, but, unfortunately, the AA′BB′ pattern could not be solved unambiguously. The values quoted in Table III for $J(AB)$ and $J(AB')$ should be considered tentative only as they are obtained from an approximate analysis assuming that $J(AA') \approx J(BB')$ and $J(AB') \approx 0$. Other as-

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[16] Brown, M. P.; Fisher, J. R.; Puddephatt, R. J.; Seddon, K. R. *Inorg. Chem.* **1979**, *18*, 2808.

[17] (a) Chatt, J.; Pombeiro, A. J. L.; Richards, R. L. *J. Organomet. Chem.* **1980**, *184*, 357 and references therein. (b) Pombeiro, A. J. L.; Carvalho, M. F. N. N.; Hitchcock, P. B.; Richards, R. L. "Abstracts", Proceedings of the 10th International Conference Organometallic Chemistry, Toronto, 1981; p 1966.

[18] Willis, S.; Manning, A. R. *J. Organomet. Chem.* **1975**, *97*, C49 and references therein.

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signments are possible but only this assignment gives values for $J(AB)$ and $J(AB')$ in close agreement with those found for **10**.

Conductivity measurements on complexes **7**–**12** demonstrated a marked solvent dependence. In dichloromethane, for example, only **8** and **10** approached the value anticipated for a 1:1 electrolyte; all others showed evidence of strong association in solution, especially **11** and **12**. In either acetone or nitromethane, however, all appeared to behave as either 1:1 or 3:1 electrolytes, as formulated.

Ligands of the type CNRR′, when monodentate, are commonly viewed as aminocarbyne ligands, in which free rotation around the C–N bond is restricted through a degree of multiple C,N bonding. In keeping with this more or less established convention, it is convenient to regard the μ-CNRR′ moieties in complexes **7**–**12** as bridging carbyne ligands that contribute three electrons to the cluster as a whole. It should not be overlooked, however, that an alternative way of regarding these complexes is as dimetalated iminium salts, in which the $[\mu\text{-CNRR}']^+$ fragment functions as a two-electron donor to the cluster. In view of the physical and structural properties exhibited by similar complexes such as **1**, **2**, and $Pt_2Cl_2(\mu\text{-CO})(\mu\text{-dppm})_2$,[8] this may well be the more appropriate convention to use.

The platinum(I) isocyanide dimers **3**, **4**, and **5** isolated in this study are of interest for a number of reasons. Of most interest to us is their reactivity toward electrophiles and nucleophiles, which should furnish information concerning the nature of the HOMOs and LUMOs in these complexes. We are continuing our research into the chemistry of complexes **3**–**5** which will be reported in subsequent publications.

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Registry No. **1**, 87101-07-3; **2**, 87101-18-6; **3**, 87101-09-5; **4**, 87101-11-9; **5**, 87101-13-1; **6**, 87101-15-3; **7**, 87101-16-4; **8**, 87101-17-5; **9**, 87101-19-7; **10**, 87114-15-6; **11**, 87114-16-7; **12**, 87101-21-1; $Pt_2Cl_2(\mu\text{-dppm})_2$, 61250-65-5; $Pt_2I_2(\mu\text{-dppm})_2$, 61289-07-4.

Direct Synthesis of Pentaphenylcyclopentadienyl Complexes of Palladium

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A series of pentaphenylcyclopentadienyl complexes of palladium(II) of the type $(\eta^5\text{-C}_5\text{Ph}_5)(\eta^3\text{-all})\text{Pd}$ (all = allyl, 2-chloroallyl, 2-methylallyl, 1-methylallyl, 1,1-dimethylallyl, 1-carbomethoxyallyl) have been prepared in high yield from the reaction of NaC_5Ph_5 with $[(\eta^3\text{-all})\text{PdCl}]_2$ in THF. Reaction of $(\eta^5\text{-C}_5\text{Ph}_5)(\eta^3\text{-all})\text{Pd}$ with phosphorus donor ligands results in the formation of zerovalent palladium complexes and coupled organic products. Reaction of $(\eta^5\text{-C}_5\text{Ph}_5)(\eta^3\text{-2-chloroallyl})\text{Pd}$ with PR_3 ligands gives a series of complexes $(\eta^5\text{-C}_5\text{Ph}_5)\text{PdCl}(\text{PR}_3)$ that are not synthetically accessible from the reaction of NaC_5Ph_5 with $[PdCl_2(PR_3)]_2$. Pyrolysis of $(\eta^5\text{-C}_5\text{Ph}_5)(\text{2-chloroallyl})\text{Pd}$ gives allene and the chloro-bridged dimer $[(\eta^5\text{-C}_5\text{Ph}_5)\text{PdCl}]_2$. Reduction of this dimer by activated zinc dust in the presence of RC≡CR′ or CO gives the palladium(I) dimers $(\eta^5\text{-C}_5\text{Ph}_5)_2(\mu\text{-RC}{\equiv}\text{CR}')\text{Pd}_2$ and $(\eta^5\text{-C}_5\text{Ph}_5)_2(\mu\text{-CO})_2\text{Pd}_2$, respectively.

Introduction

The ability of the pentamethylcyclopentadienyl ligand to enhance the stability and solubilities of various transition-metal complexes relative to their unsubstituted cyclopentadienyl analogues has been extensively utilized in recent years.[1-5] In contrast only a few complexes of the corresponding pentaphenylcyclopentadienyl ligand have been reported. These include the complex $(\eta^5\text{-C}_5\text{Ph}_5)\text{Fe(CO)}_2\text{Br}$ from the reaction of $Fe(CO)_5$ and C_5Ph_5Br,[6] $(\eta^5\text{-C}_5\text{Ph}_5)_2\text{Ni}$ from the reaction of the pentaphenylcyclopentadienyl radical (C_5Ph_5) with $Ni(COD)_2$,[7] $(\eta^5\text{-Ph}_5\text{C}_5)_2\text{Mo}$ (in low yield) from PhC≡CPh and $Mo(CO)_6$ heated under pressure,[8] and the palladium(I) dimer $(\mu\text{-PhC}{\equiv}\text{CPh})(\eta^5\text{-C}_5\text{Ph}_5)_2\text{Pd}_2$ obtained from the reaction of PhC≡CPh with palladium acetate in methanol.[9] Recent studies of $(\mu\text{-PhC}{\equiv}\text{CPh})(\eta^5\text{-C}_5\text{Ph}_5)_2\text{Pd}_2$ have shown that $\eta^5\text{-C}_5\text{Ph}_5$ complexes may frequently be markedly more stable than their $\eta^5\text{-C}_5\text{H}_5$ analogues and that the $\eta^5\text{-C}_5\text{Ph}_5$ ligand is capable of "stabilizing" various "unusual" oxidation states.[9,10] However, an obvious difficulty impeding the development of transition-metal pentaphenylcyclopentadienyl chemistry is the lack of useful synthetic routes. In particular the steric bulk of the $C_5Ph_5^-$ anion effectively reduces its nucleophilicity with respect to ligand (e.g., chloride) substitution at metal complexes, and consequently many synthetic pathways available in cyclopentadienyl chemistry fail to give complexes when using $C_5Ph_5^-$. To date no pentaphenylcyclopentadienyl transition-metal complex has been prepared directly from the $C_5Ph_5^-$ anion. This paper reports a direct entry into pentaphenylcyclopentadienyl complexes of palladium(II) and palladium(I) starting from (pentaphenylcyclopentadienyl)sodium.

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