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Synthesis and Characterization of a Mixed Metal A-Frame Complex: $Pd_2(\mu\text{-}Pt(PPh_3)_2)Cl_2(PMe_2CH_2\text{-}PMe_2)_2$

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We report the preparation of a mixed metal A-frame complex by insertion of a $Pt(PPh_3)_2$ fragment into the Pd–Pd single bond of $Pd_2Cl_2(dmpm)_2$ (dmpm = bis-(dimethylphosphino)methane). The 'isolobal' relationship between CH_2 and d^{10} ML_2 metal fragments led Hoffman and Hoffmann in 1981 to predict the existence of A-frame complexes which contain ML_2 bridgeheads [1, 2]. Recently two reports of homo-trinuclear A-frame complexes of this type have appeared. Yamamoto has described the preparation of $[M_2(\mu\text{-}M(CNR)_2)(CNR)_2(dppm)_2][PF_6]_2$ (R = 2,6-$Me_2C_6H_3$; M = Pd, Pt) by metal fragment insertion into the M–M bonds of $[M_2(CNR)_2(dppm)][PF_6]_2$ complexes [3]. Grundy has reported the isolation and structure of $[Rh_3(\mu\text{-}CO)_3(CO)_3(dppm)_2]ClO_4$ (dppm = bis(diphenylphosphino)methane) [4]. We report the synthesis of the first heteronuclear A-frame complex, $Pd_2(\mu\text{-}Pt(PPh_3)_2)Cl_2(dmpm)_2$ from $Pd_2Cl_2(dmpm)_2$ and $Pt(PPh_3)_2(C_2H_4)$.

Experimental

A solution of 0.1 g (0.18 mmol) $Pd_2Cl_2(dmpm)_2$ [5] in 25 ml absolute ethanol was added to a 50 ml flask containing 0.1396 g (0.18 mmol) $Pt(PPh_3)_2(C_2H_4)$ [6, 7]. In order to remove C_2H_4 evolved during the reaction a stream of N_2 was passed over the solution. After 21 h, the resulting dark brown solution was filtered to separate insoluble material and the filtrate was concentrated under reduced pressure. Ether was added to facilitate precipitation, and the solution was cooled at -10 °C for 6 h. A black solid was obtained and dried under vacuum, yield 40%.

All manipulations were performed under a N_2 atmosphere using Schlenk techniques. ^1H NMR and $^{31}P\{^1H\}$ NMR spectra were recorded on a Varian XL-200 spectrophotometer. ^1H and ^{31}P NMR chemical shifts were referenced to TMS and 85% H_3PO_4 respectively.

Results and Discussion

The metal–metal bond of the complex $Pd_2Cl_2(dmpm)_2$ has been shown previously to be highly reactive toward the addition of small molecules, e.g. CO, CNR, CS_2, SO_2 [8]. A related μ-CH_2 complex of Pt, $Pt_2(\mu\text{-}CH_2)Cl_2(dppm)_2$, also established the viability of methylene bridged A-frame complexes [9]. Together, the reactive Pd–Pd bond of $Pd_2Cl_2(dmpm)_2$ and the isolobal analogy between $Pt(PPh_3)_2$ and CH_2 [1, 2] provided the impetus for our synthesis of a $Pt(PPh_3)_2$ bridged A-frame complex, $Pd_2(\mu\text{-}Pt(PPh_3)_2)Cl_2(dmpm)_2$.

The complex $Pt(PPh_3)_2(C_2H_4)$ was chosen as the precursor to the 14-valence electron $Pt(PPh_3)_2$ fragment because of the known lability of the ethylene ligand [10]. The $Pt(PPh_3)_2$ fragment, however, is known to form clusters, $[Pt(PPh_3)_2]_n$ [11]. The choice of solvents for the synthesis of $Pd_2(\mu\text{-}Pt(PPh_3)_2)Cl_2(dmpm)_2$ is therefore critical. Absolute EtOH has proven to be the best of the solvents attempted inasmuch as it limits the undesirable cluster-forming reactions. The reaction of $Pd_2Cl_2(dmpm)_2$ with $Pt(PPh_3)_2(C_2H_4)$ in EtOH leads to the evolution of C_2H_4, observed by GC, and the formation of the new complex, $Pd_2(\mu\text{-}Pt(PPh_3)_2)Cl_2(dmpm)_2$. The complex has been characterized by $^{31}P\{^1H\}$ and ^1H NMR spectroscopies as the mixed metal trinuclear A-frame complex, Fig. 1.

The $^{31}P\{^1H\}$ NMR spectrum of $Pd_2(\mu\text{-}Pt(PPh_3)_2)Cl_2(dmpm)_2$ is particularly informative. The $^{31}P\{^1H\}$ NMR spectrum in EtOH solution is given in Fig. 2. A signal at -34.7 ppm is assigned to the two PPh_3 ligands coordinated to the bridgehead Pt atom. This signal exhibits a pair of ^{195}Pt satellites at -19.6 and -49.9 ppm respectively, corresponding to $^1J(Pt\text{–}P) = 2457$ Hz. The remaining signal at -25.2 ppm is approximately double the combined intensity of the Pt–PPh_3 portion of the spectrum and is assigned to the four dmpm phosphorus nuclei. The ^1H NMR spectrum of $Pd_2(\mu\text{-}Pt(PPh_3)_2)Cl_2(dmpm)_2$ reveals the presence of the PPh_3 phenyl groups (7.50 ppm, m) and two dmpm methyl environments (1.69 ppm, s; 1.60 ppm, s) in the expected overall ratio of integrated intensities, 5:4. The appearance of the dmpm $^{31}P\{^1H\}$ signal as a singlet together

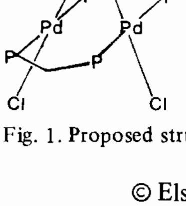

Fig. 1. Proposed structure of $Pd_2(\mu\text{-}Pt(PPh_3)_2)Cl_2(dmpm)_2$.

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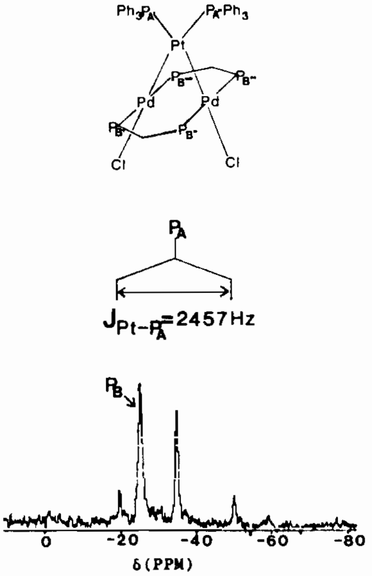

Fig. 2. $^{31}P\{^1H\}$ NMR spectrum of $Pd_2(\mu\text{-}Pt(PPh_3)_2)Cl_2(dmpm)_2$.

with two ^1H NMR methyl signals are in agreement with the NMR data for other symmetric dmpm bridged di-palladium A-frame complexes [8].

The complex $Pd_2(\mu\text{-}Pt(PPh_3)_2)Cl_2(dmpm)_2$ is the first example of a mixed metal A-frame complex. The complex however is quite unstable, thus complicating studies of its reactivity. The instability of the complex has also contributed to our lack of success in growing X-ray quality crystals to date. The instability of the complex is attributed to weak Pd–Pt bonding. The necessary *cis*-disposition of the ligands of the $Pt(PPh_3)_2$ fragment may create unfavorable steric interactions. We note that the $[Pd_2(\mu\text{-}Pd(CNR)_2)(CNR)_2(dppm)_2][PF_6]_2$ ($R = 2,6\text{-}Me_2C_6H_3$) complex reported by Yamamoto [3] appears to be quite stable. The stability of the $Pd(CNR)_2$ bridged system *versus* our $Pt(PPh_3)_2$ bridged A-frame complex may reflect the lesser steric requirements of *cis*-aryl isocyanide relative to *cis*-triphenylphosphine ligands. Electronic effects may also contribute to the lack of stability of $Pd_2(\mu\text{-}Pt(PPh_3)_2)Cl_2(dmpm)_2$ compared to $[M_2(\mu\text{-}M(CNR)_2)(CNR)_2(dppm)_2][PF_6]_2$ (M = Pd, Pt). In general, dmpm bridged Pd A-frames formed by insertion of electrophiles (CO, CNMe, SO_2, CS_2) into a Pd–Pd bond appear to be more stable than their dppm bridged counterparts [8]. This is very likely a result of the increased donor ability of dmpm compared to dppm. The $Pt(PPh_3)_2$ fragment however, may not be sufficiently electrophilic to benefit from the increased electron density of a dmpm bridged di-palladium complex.

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