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REACTIONS OF TRIALKYLMETHYLENEPHOSPHORANES WITH 1,5-CYCLOOCTADIENE-PLATINUM(II) AND -IRIDIUM(I) COMPLEXES

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Summary

The reactions of $(CH_3)_3PCH_2$ and $CH_3[(CH_3)_3C]_2PCH_2$ with $(COD)Pt(CH_3)_2$ result in the formation of the corresponding *cis*-dimethylplatinum(II)-bis-ylide complexes. With $(COD)PtCl_2$, a transylidation takes place, but the expected chelating ylide complexes cannot be isolated. Treatment of $(COD)_2Ir_2Cl_2$ with excess $CH_3[(CH_3)_3C]_2PCH_2$ gives the mononuclear ylide chelate $(COD)Ir(CH_2)_2P[C(CH_3)_3]_2$.

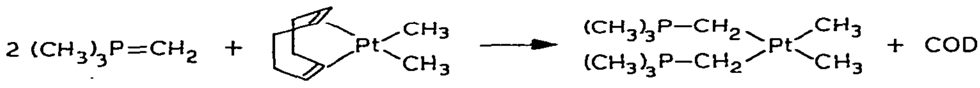
Introduction

Complexes of phosphorus ylides with transition metals are of current interest, since a number of compounds of this type are likely to be novel efficient catalysts [1—6]. The analysis of pertinent previous studies with the smallest ylide, $(CH_3)_3PCH_2$, and of a homologue which bears two bulky substituents, $CH_3[(CH_3)_3C]_2PCH_2$, suggests that ylide reactions with $(COD)Pt(CH_3)_2$, $(COD)PtCl_2$, and $[(COD)IrCl]_2$ will give complexes of these noble metals [7—10].

Results

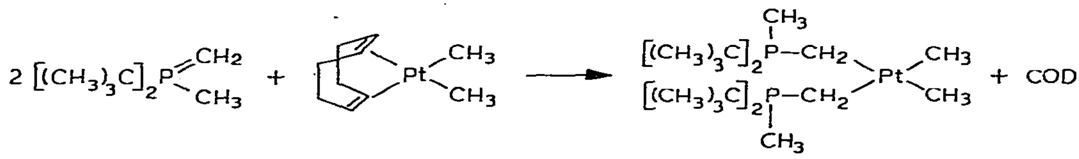
1. Platinum complexes

1.1 Compounds of type $(R'_2RPCH_2)_2Pt(CH_3)_3$ ($R' = R = Me$; $R' = tBu$). Treatment of methylenetrimethylphosphorane [7] with (1,5-cyclooctadiene)-dimethylplatinum(II) [8] in benzene in a molar ratio of 2/1 gives *cis*-bis[trimethylphosphoniummethylid]dimethylplatinum(II), I, by displacement of cyclooctadiene (COD):



(I)

When the mixture is cooled, a white solid precipitates which is easily separated by filtration. Even upon stirring the reaction mixture for several hours no evolution of methane or ethane is oberved *. Treatment of (COD)Pt$(CH_3)_2$ with t-$Bu_2MeP=CH_2$ in benzene gives the analogous 2/1 platinum complex (II):



(II)

Again no methane is liberated and ring closure does not occur. Complex II can be recrystallized from toluene at low temperatures and is isolated as a white solid. The compound is more sensitive to air and more thermolabile than I and decomposes slowly in benzene solution.

Complex I decomposes rapidly in dichloromethane, and so its NMR spectra must be recorded in THF-d_8. The ^{1}H-NMR spectrum shows two doublets accompanied by platinum satellites. One of these can be assigned to the methylplatinum protons at 0.1 ppm with a ^4J(PCPtCH) coupling of 2.2.Hz and a ^2J(PtCH) coupling of 73.12 Hz; the second group of doublets is assigned to the methylene protons at 0.7 ppm with a ^2J(PCH) coupling of 12.75 Hz and a ^2J(PtCH) coupling of 55.5 Hz. The phosphorus methyl protons give rise to a doublet at 1.94 ppm with a ^2J(PCH) coupling of 13.5 Hz. Phosphorus decoupling simplifies the signals to singlets which are still associated with the corresponding platinum satellites. ^{31}P-NMR Spectra reveal a singlet centered at 17.34 ppm with satellites ^2J(PC^{195}Pt) 91.55 Hz.

There is no evidence that the *cis* arrangement of ligands postulated in I rearranges to *trans*. Generally, the *trans* form has higher ^2J(PtCH) absolute value than the *cis*; the exact geometry, however, must await an X-ray structural analysis [12].

The ^{1}H-NMR spectrum of compound II is somewhat more complicated because of overlapping by the additional doublet of the t-butyl protons at 0.6 ppm, ^3J(PCCH) 12.8 Hz, but all other signals are as observed for I. The results are listed in Table 1. A ^{31}P-resonance appears as a singlet at 51.9 ppm with satellites of the ^2J(^{195}PtP) coupling of 91.9 Hz. The mass spectra of compounds I and II exhibit the molecular ions at *m/e* = 405 and 573, respectively.

1.2 Reactions with (COD)PtCl₂. Treatment of (COD)PtCl_2 [8] with four equivalents of t-$Bu_2MeP=CH_2$ generates an orange-yellow solution. The expected amount of di-t-butyldimethylphosphonium chloride is precipi-

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* In contrast, $[Me_3Pt^{IV}]^+ PF_6^-$ and $CH_2=PPh_3$ readily lose ethane and methane [11].

TABLE 1

NMR-DATA OF COMPLEXES I, II AND III [a]

I	^{1}*H-NMR* (THF-d_8): $\delta(CH_3) = 1.9$, d, 18 H, $^2J(PCH) = 13.5$; $\delta(CH_2) = 0.7$, "d", 4 H, $^2J(PCH) = 12.75$, $^2J(^{195}PtCH) = 55.5$; $\delta(PtCH_3) = 0.1$, "d", 6 H, $^4J(PC^{195}PtCH) = 2.2$, $^2J(^{195}PtCH) = 73.1$; $\{^{31}P\}$: s, s, s with satellites. ^{31}P $\{^1H\}$-*NMR* (THF-d_8): $\delta(P) = 17.3$, s, $^2J(PtP) = 91.55$
II	^{1}*H-NMR* (C_6D_6): $\delta(CH_3) = 0.9$, d, 6 H, $^2J(PCH) = 12.4$; $\delta(CCH_3) = 0.6$, d, 36 H, $^3J(PCCH) = 12.5$; $\delta(CH_2) = 0.42$, "d", 4 H, $^2J(PCH) = 11.5$, $^2J(^{195}PtCH) = 46.0$; $\delta(PtCH_3) = 0.2$, "d". 6 H, $^4J(PCPtCH) = 1.9$, $^2J(^{195}PtCH) = 51.5$. $\{^{31}P\}$: s, s, s, s, with satellites. ^{31}P $\{^1H\}$-*NMR* (C_6D_6): $\delta(P) = 51.9$, s, $^2J(PtP) = 91.9$ Hz.
III	^{1}*H-NMR* (C_6D_6): $\delta(CH_2P) = 0.51$, d, 4 H, $^2J(PCH) = 4.5$; $\delta(CCH_3) = 1.09$, d, 18 H, $^3J(PCCH) = 12.75$; $\delta(C_8H_{12}) = 1.75$–2.6, m, 8 H, and 4.0, m, 4 H. $\{^{31}P\}$: s, s, m, m. ^{13}C $\{^1H\}$ *NMR* (C_6D_6): $\delta(CH_2) = -20.06$, d, $^1J(PC) = 29.28$, $\delta(CH_3) = 26.55$, s; $\delta(PCC) = 30.16$, d, $^1J(PC) = 11.6$; $\delta(C_8H_{12}) = 32.81$, s, and 63.12 s. ^{31}P $\{^1H\}$*NMR* (C_6D_6): $\delta(P) = 79.53$, s.

[a] Chemical shifts in ppm. Coupling constants in Hz.

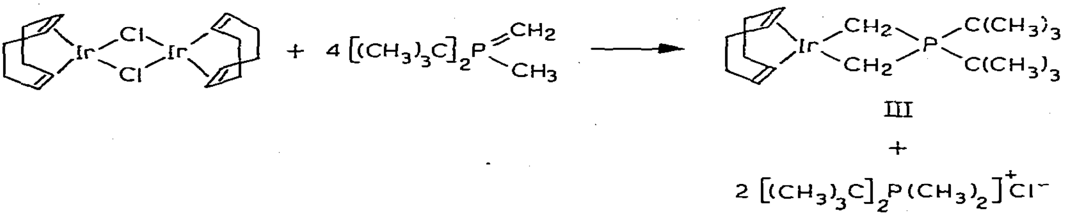
tated and separated by filtration. This salt was identified with NMR and IR spectra by comparison with an authentic sample.

^{1}H-NMR spectra of the supernatant solution (benzene) show signals which can be assigned to t-butyl and methylene protons in the expected range of chemical shifts, but no pure well-defined compound can be isolated. However, removal of the solvent from the coloured benzene solution gives a red-brown oily product which has a complex NMR spectrum.

All efforts to obtain a pure solid by recrystallisation from solvents such as toluene, pentane or ether failed. Though transylidation occurs, no well defined Pt-complex is isolated in this way; even at low temperatures the reaction route is the same.

2. *Iridium Compounds.*

Dimeric $[(1,5\text{-COD})IrCl]_2$ [13] is treated with $t\text{-}Bu_2MeP{=}CH_2$ in benzene solution in a molar ratio of 1/2. Transylidation immediately gives the expected iridium complex (III) as well as the precipitated phosphonium salt:



The phosphonium salt is filtered off, the orange-red filtrate evaporated, and the residue recrystallized from toluene. The red crystals obtained are extremely sensitive to moisture and air and decompose to paramagnetic, purple Ir^{III} species.

The ^{1}H-NMR spectrum of the product shows, besides the two complex signals of the coordinated cyclooctadiene, two doublets of the methylene and t-butyl protons. ^{31}P Decoupling simplifies the signals to singlets. The ^{13}C-NMR spectrum supports the proposed structure. Proton decoupled ^{31}P resonance shows a singlet at δ 79.5 ppm downfield relative to H_3PO_4. The mass-spectrum indicates the monomeric molecular ion at $m/e = 473$.

Conclusion

$Me_3P{=}CH_2$ and t-$Bu_2MeP{=}CH_2$ react with (COD)$Pt(CH_3)_2$ by substitution of cyclooctadiene to give the bis-monodentate ylide complexes I and II. No deprotonation of the ylide is observed even in the case of the bulky t-butyl substituted ylide. Starting from (COD)$PtCl_2$ and t-$Bu_2MeP{=}CH_2$ the expected transylidation is indeed observed, but the product formed in solution decomposes on attempted isolation.

From [(COD)IrCl]$_2$ and t-$Bu_2MeP{=}CH_2$ the new chelated ylide complex III is formed; this is analogous to known (COD)rhodium(I) ylide complexes. The reaction route involves the transylidation mechanism.

Experimental

Preparation of $(Me_3PCH_2)_2Pt(CH_3)_2$ *(I)*

0.36 g (1.08 mmol) (COD)$Pt(CH_3)_2$ is dissolved in benzene and a solution of 0.195 g (2.16 mmol) of $Me_3P{=}CH_2$ in benzene is slowly added. The mixture is stirred at room temperature for 1 h. The white precipitate which forms on cooling is filtered off, washed, and dried in vacuo, giving I in 86% yield (0.370 g, 0.9 mmol), m.p.: 154°C. Anal. Found: C, 30.12; H, 7.11; P, 15.12; $C_{10}H_{28}P_2Pt$ Calcd.: C, 29.7; H, 6.96; P, 15.3. Mass spectrum: $m/e = 405$.

Preparation of $(t\text{-}Bu_2MePCH_2)_2Pt(CH_3)_2$ *(II)*

0.35 g (1.05 mmol) (COD)$Pt(CH_3)_2$ and 0.51 g (2.9 mmol) t-$Bu_2MeP{=}CH_2$ are brought into reaction in the same way, with stirring for 12 h at room temperature and 2 h at 60°C. The solvent is removed and the crude product recrystallized from toluene at —78°C. II is obtained in 56% yield (0.34 g, 0.7 mmol) as a white solid. m.p.: 180°C, (decomp). Anal. Found: C, 46.13; H, 9.41, $C_{22}H_{52}P_2Pt$ Calcd.: C, 46.06; H, 9.14. Mass spectrum: $m/e = 573$.

Preparation of $(C_8H_{12})Ir(CH_2)_2P(tBu)_2$ *(II)*

To a solution of 0.40 g (0.65 mmol) (1,5-cyclooctadiene)iridium(I) chloride dimer in 10 cm^3 of benzene, a solution of 0.52 g (3 mmol) of $tBu_2MeP{=}CH_2$ in benzene is added dropwise. The mixture is stirred for 2 h at room temperature. The precipitated phosphonium salt is filtered off, and the solvent removed in vacuo. Recrystallization from toluene at —78°C gives III as orange-red, extremely air sensitive crystals, m.p.: 98°C. Anal. Found: C, 45.21; H, 6.94; $C_{18}H_{34}IrP$ Calcd. C, 45.65; H, 7.24; Mass spectrum: $m/e = 473$ (65%).

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