Journal of Organometallic Chemistry, 371 (1989) 15–18
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
JOM 09905

Bifunctional ligands for the preparation of heterobinuclear complexes. Synthesis and characterization of $Tl(C_5H_4)P(CH_3)_2$, $[(\eta^5\text{-}C_5H_4)P(CH_3)_2]_2ZrCl_2$ and the heterobinuclear complex $\{[\mu\text{-}(\eta^5\text{-}C_5H_4)P(CH_3)_2]ZrCl_2\}Mo(CO)_4$

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(Received January 12th, 1989)

Abstract

The synthesis and spectroscopic characterization of the bifunctional ligand $Tl(C_5H_4)P(CH_3)_2$, the ring functionalizd metalloligand, $[(\eta^5\text{-}C_5H_4)P(CH_3)_2]_2ZrCl_2$, prepared from it and the heterobinuclear complex, $\{[\mu\text{-}(\eta^5\text{-}C_5H_4)P(CH_3)_2]_2ZrCl_2\}Mo(CO)_4$, are reported. This heterobifunctional ligand will complement work with metallocene complexes of $(C_5H_4)PPh_2$ because of the smaller steric demands and anticipated higher basicity of the dimethylphosphine unit compared to the diphenylphosphine group.

This group has been interested in ring-functionalized group 4 metallocenes, $[(C_5H_4)PR_2]_2ZrXY$, as metalloligands for the synthesis of heterobinuclear complexes [1]. We have previously reported the synthesis of the complexes where R = Ph and X = Y = Cl and its complex with $Mo(CO)_4$. More recently, we have prepared metalloligands where methyl ligands have been substituted for the chlorides on the zirconium atom and complexes of these new metalloligands with Pt^{II} and Pt^{IV} [2]. That work suggested that substitution at zirconium has little effect upon the basicity of the phosphine ligand. In order to change the basicity and steric bulk of the phosphine we are preparing bifunctional ligands $(C_5H_4)PR_2$ where R is an alkyl group. Herein is reported the synthesis and spectroscopic characterization of $Tl(C_5H_4)P(CH_3)_2$ (I), the zirconium metalloligand, $[(\eta^5\text{-}C_5H_4)P(CH_3)_2]_2ZrCl_2$ (II), and the heterobinuclear complex of II with $Mo(CO)_4$.

The synthesis of $Tl(C_5H_4)P(CH_3)_2$ is similar to that used by Rausch for $Tl(C_5H_4)PPh_2$ [3], deprotonation of dimethylphosphinocyclopentadiene. Mathey had previously reported that dimethylphosphinocyclopentadiene was unstable, but

0022-328X/89/$03.50

could be used in situ [4]. The addition of $P(CH_3)_2Cl$ to an ether suspension of $Tl(C_5H_5)$ resulted in the formation of thallium chloride and the dimethylphosphinocyclopentadiene [5*].

$$Tl(C_5H_5) + P(CH_3)_2Cl \rightarrow (C_5H_5)P(CH_3)_2 + TlCl$$

The thallium chloride is removed by filtration and the resulting clear, colorless solution is treated with one equivalent of thallium ethoxide:

$$(C_5H_5)P(CH_3)_2 + TlOC_2H_5 \rightarrow Tl(C_5H_4)P(CH_3)_2$$

Vigorous stirring yields a nearly colorless solid which is collected by filtration. The crude material can be vacuum sublimed (0.6 mtorr, 60 °C) to give analytically pure material [6*] in 60% yield based on TlCp. Proton and phosphorus NMR data are in Table 1. The phosphorus atom resonance of this bifunctional ligand appears at higher field (−63.3 ppm) than the corresponding diphenyl compound (−18.3 ppm) [3].

This bifunctional ligand readily reacts with $ZrCl_4 \cdot 2(C_4H_8O)$ in toluene to give the ring functionalized zirconacene dichloride, $[(\eta^5\text{-}C_5H_4)P(CH_3)_2]_2ZrCl_2$:

$$2\ Tl(C_5H_5) + ZrCl_4 \cdot 2(C_4H_8O) \xrightarrow[\text{toluene}]{24\text{ h}} \left[(\eta^5\text{-}C_5H_4)P(CH_3)_2\right]_2ZrCl_2 + 2\ TlCl$$

Filtration to remove thallium chloride and washing with pentane gives the product in about 95% purity. The ring functionalized zirconacene can be sublimed (0.5 mtorr, 75 °C) to give the bright yellow air sensitive product as analytically pure material [7*] in 80% yield based on $Tl(C_5H_4)P(CH_3)_2$. Proton and phosphorus NMR data are in Table 1. These show little difference (small downfield shifts of all signals) from those of the bifunctional ligand as the thallium salt.

This metalloligand readily displaces piperidine from bis(piperidine)tetracarbonylmolybdenum(0) in toluene to give the bimetallic complex, $\{[\mu\text{-}(\eta^5\text{-}C_5H_4)P(CH_3)_2]_2ZrCl_2\}Mo(CO)_4$ (III) in 85% yield. This complex may be recrys-

$$\left[(\eta^5\text{-}C_5H_4)P(CH_3)_2\right]_2ZrCl_2 + (pip)_2Mo(CO)_4 \rightarrow \left\{\left[\mu\text{-}(\eta^5\text{-}C_5H_4)P(CH_3)_2\right]_2ZrCl_2\right\}Mo(CO)_4$$
$$\text{(III)}$$

Table 1

^1H and ^{31}P NMR data for the $(C_5H_4)P(CH_3)_2$ ligand and its complexes

Species	$\delta(^1H)$		$\delta(^{31}P)\{^1H\}$
	$\delta(C_5H_4)$	$\delta(PCH_3)$ $J(P\text{-}H)$ (Hz))	
I [a]	6.07(m,4H), 6.23(m,4H)	0.99(d,12H) (3.0)	−63.3(s)
II [b]	6.35(m,4H) 6.15(m,4H)	1.04(d,12H) (3.4)	−53.4(s)
III	6.07(m,4H), 6.10(m,4H)	1.28(d,12H) (5.8) [c]	−8.6(s)

[a] In toluene-d_8. [b] In benzene-d_6. [c] Filled in doublet.

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* Reference numbers with asterisks indicate notes in the list of references.

tallized from pentane/toluene or dichloromethane. The orange crystals obtained from these solvents lose solvent to give the product as a yellow powder [8*]. The infrared spectrum in the C–O stretching region is consistent with a *cis*-$L_2Mo(CO)_4$ complex [9*]. These frequencies are quite similar to those of *cis*-$L_2Mo(CO)_4$ where L = $PPhMe_2$ and PPh_2Me [10] and the heterobimetallic complex where $L_2 = [(\eta^5\text{-}C_5H)PPh_2]_2ZrCl_2$ [2]. These results suggest that the ring functionalized zirconacene acts much as a nonmetal bearing chelating phosphine with little effect from the zirconium atom being transmitted to the phosphorus atom. The small shifts of the C–O stretching frequencies from the diphenylphosphino-functionalized zirconacene suggests that the donor properties of the phosphines of this new metalloligand are not very different from other tertiary phosphines, at least in their $Mo(CO)_4$ complexes.

Multinuclear NMR measurements on III in CD_2Cl_2 at ambient temperature are also consistant with the formulation of a *cis*-diphosphinetetracarbonylmolybdenum(0) complex. The phosphorus spectrum shows a single resonance shifted downfield from the uncoordinated metalloligand. The proton NMR spectrum shows two multiplets in the cyclopentadienyl region and a filled-in doublet for the phosphine methyl groups. These results show that each ring is equivalent on the NMR time scale and that the α and β protons on the ring are rendered equivalent, either because of the conformation of the complex, coincidental chemical shifts or by a fluxional process. The ^{13}C NMR spectrum shows that the α carbons and the β carbons are equivalent on the NMR time scale as well [11], as seen in the proton NMR.

In addition, the carbonyl carbons are observed as two resonances as expected for a *cis*-diphosphinemetal tetracarbonyl species. The *cis*-CO carbons appear as a triplet at δ 210.2 ((J(P–C) 10 Hz) and the *trans*-CO ligands appear as a doublet of doublets at δ 214.76 ($J(P_{cis}\text{–}C)$ 7.1 Hz, $J(P_{trans}\text{–}C)$ 8.8 Hz). These data are consistant with a *cis*-diphosphinetetracarbonylmolybdenum(0) species and indicate that if fluxional processes are occurring, they do not involve phosphine dissociation from the Mo coordination sphere, a result which is consistant with prior work [12]. We are currently working to determine the solid state and solution structures of this complex.

Conclusions

The syntheses of the bifunctional ligand $Tl[(C_5H_5)P(CH_3)_2]$ and the ring functionalized zirconacene dichloride metalloligand derived from it have been accomplished. This new metalloligand forms a complex with the $Mo(CO)_4$ fragment in which the phosphine ligands are *cis*. The ability of this metalloligand to bind other metal complex fragments and the substitution of the chloride ligands on the metalloligand are currently under investigation.

Acknowledgements

The purchase of the Bruker AM-400 NMR Spectrometer was supported in part by PHS grant RR-08101 from the NIH-MBRS program, NSF Grant DMB-8503839 and grants from the W.M. Keck Foundation and the Camille and Henry Dreyfus Foundation. Acknowledgement is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society for support of this research.

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5 All steps described were performed under an atmosphere of purified argon or using vacuum techniques.

6 Analysis: Found: C, 25.73; H, 3.22. $C_7H_{10}PtI$ calcd.: C, 25.32; H, 3.06%.

7 Analysis. Found: C, 40.71; H, 4.83. $C_{14}H_{20}P_2Cl_2Zr$ calcd.: C, 40.78; H, 4.89%.

8 Analysis. Found: C, 34.5; H, 3.11. $C_{18}H_{20}O_4P_2Cl_2ZrMo$ calcd.: C, 34.85; H, 3.25%.

9 Absorptions in CH_2Cl_2 solution at: 2021(m), 1920(s), 1900(s), 1885(sh) cm^{-1}.

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