

Preparation and Characterization of Ni(II), Co(II) and Cr(III) Complexes with Benzoylmethylenetriphenylphosphine

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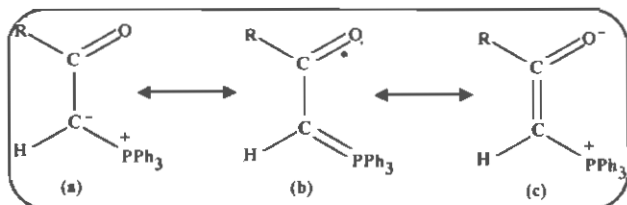
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ABSTRACT: The reaction between Ni(II), Co(II), Cr(III) nitrates, Ni(II) chloride and ambidentate α -keto ylide benzoylmethylenetriphenylphosphine (BPPY) resulted in isolation of $[\text{Ni}(\text{BPPY})_2](\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$, $[\text{Ni}(\text{BPPY})_2]\text{Cl}_2$, $[\text{Co}(\text{BPPY})_2](\text{NO}_3)_2$ and $[\text{Cr}(\text{BPPY})_3](\text{NO}_3)_3 \cdot 2\text{H}_2\text{O}$. The compounds were characterized by elemental analyses and infrared ^1H NMR spectroscopy, molar conductivity in solution and molecular weight measurements.

KEY WORDS: Complex, Benzoylmethylenetriphenylphosphine, Ni(II), Co(II), Cr(III)

INTRODUCTION

The chemistry of transition metal complexes of ambidentate ylide ligands containing phosphorus, arsenic and sulfur have aroused many interests in recent years. The benzoylmethylenetriphenylphosphorane ligand has three resonance forms as in Scheme 1, which may coordinate to a transition metal through different sites; ylide's methine carbon atom (1a), or the carbonyl oxygen atom (1c) and produce different complexes.



Scheme 1: Resonance forms for carbonyl stabilized ylides

The literature has examples of complexes in which the ylide is O-bonded [1,2], C-bridging [2], or C-bonded with orthometalation [3]. Since both reactivity

and the stretching frequency of carbonyl (ν_{CO}) are related to charge delocalization on the phosphorus ylide, the reactivity could be predicted from infrared data. Soft metal centers such as Pt(II), Pd(II) and Hg(II) would preferentially bond through the methine carbon atom, Scheme (1a), leading to an increase in the carbonyl stretching frequency [4,5]. This has been confirmed by x-ray structure determination of binuclear complex $[\text{Pt}(\mu\text{-Cl})\text{CH}_3\text{COCHP}(\text{C}_6\text{H}_4)(\text{C}_6\text{H}_5)_2]_2$ [3], in which one of the phenyl groups from triphenylphosphine coordinates with platinum forming orthometalation species [4]. Hard metal centers such as Ni(II) and Co(II) are generally coordinated through carbonyl oxygen atom, Scheme (1c). But the reaction of the ylide with the anhydrous metal halides in acetonitrile led to protonation of the ylide to give $[\text{ylide-H}]_2^+[\text{MCl}_4]^{2-}$ [6].

Three complexes of group IV metals Ti(IV), Zr(IV) and Hf(IV) with acetylmethylenetriphenylphosphine (APPY) and benzoylmethylenetriphenyl-

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phosphine (BPPY) ligands of the type MCl_4 (ylide) (THF) have been reported wherein the ylides have been bound through carbonyl oxygen atom. The stretching frequency of carbonyl oxygen atom in the ylide has been shifted to lower energy ($12-18\text{ cm}^{-1}$) in the IR spectrum and the x-ray diffraction study of a single crystal of $[TiCl_4(APPY)_3(THF)]$. THF complex has confirmed the IR data [1]. ^{31}P , ^{13}C , 1H NMR spectroscopy also suggested that ligands were coordinated through the carbonyl oxygen atom.

Facchin et al. have shown that Pd(II) complexes of acetylmethylenetriphenylphosphine, wherein ligands were coordinated through the methine carbon atom, displayed strong absorptions in the range $1630-1634\text{ cm}^{-1}$ with $\Delta\nu = \nu_{(CO)_{coord.}} - \nu_{(CO)_{uncoord.}}$ of $101-105\text{ cm}^{-1}$ [7], behaving as hard metal centers.

RESULTS AND DISCUSSIONS

Reaction of metal ions in $NiCl_2 \cdot 6H_2O$, $Co(NO_3)_2 \cdot 6H_2O$ and $Cr(NO_3)_3 \cdot 9H_2O$ with the ylide, BPPY, resulted in isolation of new complexes $[Ni(BPPY)_2]Cl_2$, $[Ni(BPPY)_2](NO_3)_2 \cdot 2H_2O$, $[Co(BPPY)_2](NO_3)_2$ and $[Cr(BPPY)_3](NO_3)_3 \cdot 2H_2O$ respectively. Analytical data, melting points and molar conductivities are listed in Table 1. Molecular weights and water of hydrations are given in Table 2. Infrared absorption bands and 1H NMR data are summarized in Table 3.

All these complexes are stable in the solid and in solution. Their solutions in acetone are conducting. Previous studies on ylide complexes of Ag(I) nitrate and perchlorate solutions of the type $[Ag(PH_3PCHC(O))_2R]X$, ($R=OEt$, $X=ClO_4$ and $R=C_6H_5$, $X=NO_3$), in acetone showed that they were conducting ($100-135\text{ ohm}^{-1}\text{ cm}^2\text{ mol}^{-1}$). However, structural deter-

Table 1 : Analytical data, melting points and molar conductivities ($ohm^{-1}\text{ cm}^2\text{ mol}^{-1}$) in acetone

Compound	Metal	% Found (Calcd.)			m.p.(°C)	Λ_M
		C	H	N		
BPPY	—	—	—	—	179-180	—
$[Ni(BPPY)_2](NO_3)_2 \cdot 2H_2O$	5.99 (5.99)	63.70 (63.75)	4.70 (4.73)	3.5 (2.86)	205-207	—
$[Ni(BPPY)_2]Cl_2$	6.62 (6.59)	70.3 (70.14)	5.20 (4.76)	—	167-169	192
$[Co(BPPY)_2](NO_3)_2$	6.20 (6.24)	66.0 (66.17)	4.8 (4.50)	3.3 (2.97)	205-206	242
$[Cr(BPPY)_3](NO_3)_3 \cdot 2H_2O$	— —	66.2 (66.19)	4.9 (4.74)	3.0 (2.9)	172-174	290

Table 2: Molecular weights and water of hydration

Compound	Molecular weight found* (Calcd)**	No. of moles of hydration water
$[Ni(BPPY)_2](NO_3)_2 \cdot 2H_2O$	1000(997.6)	1.98=2
$[Ni(BPPY)_2]Cl_2$	888.9(890.47)	—
$[Co(BPPY)_2](NO_3)_2$	941.17(943.80)	—
$[Cr(BPPY)_3](NO_3)_3 \cdot 2H_2O$	1454.5(1415.32)	1.86=2

* Molecular weights were obtained in camphor mixture

** Water of hydration was obtained by heating the compound at $100^\circ C$

Table 3: IR absorption frequencies (cm^{-1}) and ^1H NMR data

Compound	ν_{CO}	$\Delta\nu_{\text{CO}}$	$\delta(\text{CH})$	$^2\text{J}(\text{P-H})$
BPPY	1520	—	4.35	25.5
$[\text{Ni}(\text{BPPY})_2](\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$	1665	145	7.98	8.7
$[\text{Ni}(\text{BPPY})_2]\text{Cl}_2$	1678	158	—	—
$[\text{Co}(\text{BPPY})_2](\text{NO}_3)_2$	1665	145	6.1	8.7
$[\text{Cr}(\text{BPPY})_3](\text{NO}_3)_3 \cdot 2\text{H}_2\text{O}$	1670	150	—	—
$[\text{TiCl}_4(\text{BPPY-O})(\text{THF})]^*$	1520	-16	5.25	21.60
$[\text{Ag}(\text{BPPY-C})_2]\text{ClO}_4$	1610	90	5.06	6.0

* IR stretching frequency for ν_{CO} has been reported 1536 cm^{-1} [6]

mination of nitrate complex revealed that nitrate ion was loosely associated with the metal center [8]. In these complexes the ylide ligands were bonded to the silver atom through the methine carbon atom, and the IR absorption band of carbonyl group shifted to higher frequency compared with uncoordinated ylide (Table 3).

Infrared spectroscopy has been demonstrated to be a reliable indicator of the ylide's bonding mode [1,5,9]. In our four new complexes of Ni(II), Co(II) and Cr(III) nitrates and Ni(II) chloride with benzoylmethylenetriphenylphosphine (BPPY), the ylide ligands bond to the metal atom through the methine carbon. This was indicated by the infrared spectra, wherein they exhibit an increase ($140\text{-}158 \text{ cm}^{-1}$) for ν_{CO} compared with the free ligand (Table 3).

^1H NMR data are summarized in Table 3, which display a doublet at 7.98 and 6.1 ppm for the methine proton in Ni(II) and Co(II) complexes respectively.

The $^2\text{J}(\text{P-H})=8.7 \text{ Hz}$ value resulting from methine proton interaction with the phosphorus atom of the ligand is lowered by 16.8 Hz than those for free ligand. The $^2\text{J}(\text{P-H})$ coupling constants for the coordinated ligands have been used to distinguish between O-coordination and C-(methine) coordination [1,5,8]. Complexes wherein the ylide is O-coordinated exhibit a $^2\text{J}(\text{P-H})$ value between 17-24 Hz, smaller than those observed for free ligand and are close to those for confirmed $^2\text{J}(\text{P-H})=24 \text{ Hz}$ [8-10]. Compounds wherein the ylide is C-coordinated exhibit a $^2\text{J}(\text{P-H})$ value of 6 or less Hz [3,5,6, 11-15].

Since the amount of the water in solvents being

used were not certain and the solvents were not dried for conductivity measurements, therefore from these data we will not be able to decide the number of ions or draw a general formula which will fit the data obtained. But the data show that the compounds have ionic behaviour in the solution.

EXPERIMENTAL

Infrared spectra were recorded using KBr pellet technique on a Perkin-Elmer 843. ^1H NMR spectra were taken on a Perkin-Elmer F.T 80 MHz spectrometer in CDCl_3 solvent. Elemental analyses were performed on Haraeus CHN-O-Rapid by N.I.O.C. Research Institute of Petroleum Industry, Ray, Iran. Transition metal ion measurements were performed by atomic absorption spectrophotometer Varian Tec-tron Type AA-5 model and molar conductance of compounds were measured in acetone solution with conductometer type CDM2e. Melting points were taken on a Stuart Scientific apparatus type SMP1 and are uncorrected.

Preparation of phenacylbromide

This compound was prepared by previously reported method [16].

Preparation of phenacyltriphenylphosphoniumbromide

This compound was prepared by previously reported method [16].

Preparation of triphenylphosphinebenzoylmethylene

(BPPY)

This compound was also prepared according to previously reported method [16]. Selected IR bands (KBr, cm^{-1}): 2935(w), 1595(m), 1525(vs), 1480(m), 1442(s), 1385(vs), 1185(s), 1125(s), 1060(w), 1000(s), 765(m), 750(s), 695(s), 545(vs).

Preparation of $[\text{Ni}(\text{BPPY})_2](\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$

A 250 mL flask was charged with 0.29 g (1 mmol) of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in 100 mL of THF. To this solution 0.76 g (2 mmol) BPPY solution in 20 mL THF, was added slowly. Dark-green solution changed to yellow color and the solution was stirred for 3 h. This solution was filtered and the volume reduced to 50 mL. Green-yellow crystals were washed with THF and air dried. 0.75 g complex (yield 76%) was obtained which melted at 205-207°C.

^1H NMR, in CDCl_3 : δ ppm 5.98(d, 1H, CH, $J=8.7$ Hz), 7.3-8.2(m, 20 H, C_6H_5); IR(KBr, cm^{-1}): 2996(w), 2945(s), 2812(s), 1665 (vs), 1585(m), 1475(m), 1445(s), 1375(vs), 1335(vs), 1175 (m), 1120(s), 997(s), 745(vs), 685(vs), 512(s).

Preparation of $[\text{Ni}(\text{BPPY})_2]\text{Cl}_2$

A 250 mL flask was charged with 0.29 g (1 mmol) of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ dissolved in 70 mL acetone. The green solution was stirred for few minutes and to this clear solution 0.7 g (2 mmol) of BPPY dissolved in 50 mL acetone was added slowly. This green-yellow solution was stirred for 4 h. Solution was filtered and the volume reduced to 60 mL. This solution was left at room temperature for 5 days, and the volume reached to 10 mL. Green-yellow crystals were collected, dissolved in 10 mL of dichloromethane and then 20 mL of acetone was added.

The crystals were isolated after 3 days, washed with 5 mL of acetone and air dried. The yield was 0.66 g. (74%) which melted at 167-169°C.

IR(KBr, cm^{-1}): 3557(s), 3360(s), 3085(w), 1678 (vs), 1640(s), 1595(m), 1480(m), 1435(vs), 1207(m), 1195 (m), 1115(s), 745(s), 725(s), 685(vs), 545(w), 385(s).

Preparation of $[\text{Co}(\text{BPPY})_2](\text{NO}_3)_2$

A 250 mL flask was charged with 0.29 g (1 mmol)

of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and was dissolved in 80 mL acetone, then 0.7 g (2 mmol) of BPPY solution in 30 mL of acetone was added. This solution was filtered and the filtrate was kept in refrigerator for 14 h.

The solution was filtered in a 100 mL beaker and was kept at room temperature. The violet crystals were isolated after 5 days. The crystals were collected, washed with 5 mL acetone and air dried. The yield was 0.744 g (79%). The product was recrystallized from 10 mL dichloromethane and 5 mL *n*-hexane, which melted at 205-206°C.

^1H NMR: δ ppm 6.1(d, 1H, CH, $J=8.7$ Hz), 7.3-8.2 (m, 20 H, C_6H_5); IR(KBr, cm^{-1}): 2945(w), 1665(vs), 1590(m), 1485 (m), 1385(s), 1365(vs), 1340(vs), 1200 (m), 1185(m), 1110 (s), 1035(w), 985(s), 745(vs), 680 (vs), 515(s), 490(s).

Preparation of $[\text{Cr}(\text{BPPY})_3](\text{NO}_3)_3 \cdot 2\text{H}_2\text{O}$

A 250 mL flask was charged with 0.2 g (0.5 mmol) of $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in 50 mL of absolute ethanol. This solution was stirred for 30 min and a pale green solution was obtained. 0.38 g (1 mmol) of BPPY ligand dissolved in 50 mL of ethanol was added to above solution slowly. This solution was stirred for 4 h and was filtered. The volume of the filtrate was reduced to 60 mL by suction. This solution was transferred in a 100 mL beaker and was kept in a dark place.

Green crystals were isolated after 7 days. 0.48 g (68% yield) complex was obtained which melted at 172-174°C.

IR(KBr, cm^{-1}): 3445(w), 1670(vs), 1595(m), 1480 (m), 1435(s), 1385(vs), 1360(vs), 1345(vs), 1205(m), 1185 (m), 1105(s), 995(s), 740(vs), 715(s), 680(vs), 515(s).

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REFERENCES

- [1] Albanese, J., Staley, D. L., Rheingold, A. L. and Burmeister, J. L., *J. Inorg. Chem.*, **29**, 12, 2209 (1990).
- [2] Vicente, J., Chicote, M. T., Cayuelas, J. A., Fernandez-Baeza, J., Jones, P. G., Sheldrick, G. M. and Espinet, P. E., *J. Chem. Soc. Dalton*

- Trans.*, 1163(1985).
- [3] Ilingsworth, M. L., Teagle, J. A. and Rheingold, A. L., *Organometallics*, **2**, 1364(1983).
- [4] Burmeister, J. L., Silver, J. L., Weleski, E. T., Schweizer, E. E. and Kopay, C. M., *Synth. React. Inorg. Met. Chem.*, **3**, 339(1973).
- [5] Weleski, E. T., Silver, J. L., Jansson, M. D. and Burmeister, J. L., *Organomet. Chem.*, **102**, 365 (1975).
- [6] Albanese, J. A., Staley, D. L., Rheingold, A. L. and Burmeister, J. L., *Acta Crystallogr., Sect. C.: Cryst. Struct. Commun.*, **C45**, 1128(1989).
- [7] Facchin, G., Bertani, R., Zanutto, L., Calligaris, M. and Nardin, G., *J. Organomet. Chem.*, **366**, 409 (1989).
- [8] Vicente, J., Chicote, M. T., Fernandez-Baeza, J., Martín, J., Saura-Llamas, J. and Turpin, J., *J. Organomet. Chem.*, **331**, 409(1987).
- [9] Uson, R., Fornies, J., Navarro, R., Espinet, P. and Mendivil, C., *J. Organomet. Chem.*, **290**, 125 (1985).
- [10] Buckle, J. and Harrison, P. G., *J. Organomet. Chem.*, **C17**, 49(1973).
- [11] Kawafune, I. and Matsubayashi, G., *Inorg. Chim. Acta*, **70**, 1(1983).
- [12] Teagle, J. A. and Burmeister, J. L., *Inorg. Chim. Acta*, **118**, 65(1986).
- [13] Albanese, J. A., Rheingold, A. L., and Burmeister, J. L., *Inorg. Chim. Acta*, **150**, 213 (1988).
- [14] Bravo, P., Fronza, G. and Ticcozi, C., *J. Organomet. Chem.*, **111**, 361(1976).
- [15] Onishi, M., Ohama, Y., Hiraki, K. and Shintam, H., *Polyhedron*, **1**, 539(1982).
- [16] Ramirez, F. and Dershowitz, S., *J. Org. Chem.*, **22**, 41(1957).