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Journal of Organometallic Chemistry 509 (1996) 89–93

Journal of Organometallic Chemistry

New dinuclear and heterotrinuclear complexes containing the $M_2(\mu\text{-az})(\mu\text{-PPh}_2)$ core (M = Rh or Ir; az = azolate)

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Received 8 June 1995

Abstract

The heterobridged dinuclear complexes $[M_2(\mu\text{-Pz})(\mu\text{-PPh}_2)(COD)_2]$ (M = Rh; Pz = pyrazolate (pz) (1) or 3,5-dimethylpyrazolate (dmpz) (2) (M = Ir; Pz = pz (3) or dmpz (4)) have been prepared by reaction of $[M_2(\mu\text{-Cl})(\mu\text{-Pz})(COD)_2]$ with $LiPPh_2$. Substitution of the chloride bridge in $[Rh_2(\mu\text{-Cl})(\mu\text{-PPh}_2)(COD)_2]$ by an azolate on compound is a good method for preparing complexes $[Rh_2(\mu\text{-az})(\mu\text{-PPh}_2)(COD)_2]$ (az = 1,2,4-triazolate (tz) (5), or tetrazolate (ttz) (6)). The preparation of the heterobridged heterotrinuclear complexes $[(M(\mu\text{-pz})(\mu\text{-PPh}_2)(COD))_2Pd]$ (M = Rh (7) or Ir (8)) is also reported.

Keywords: Rhodium; Azolate; Indium; Phosphide

1. Introduction

There is increasing interest on hydroformylation reactions catalyzed by dinuclear rhodium complexes [1–3]. In particular, the heterobridged dinuclear complex $[Rh_2(\mu\text{-pz})(\mu\text{-S}^t\text{Bu})(CO)_2\{P(OMe)_3\}_2]$ [4] has demonstrated a higher activity than the related homobridged complex $[Rh_2(\mu\text{-pz})_2(CO)_2\{P(OMe)_3\}_2]$ [5]. However, Blum and coworkers have reported the preparation of the heterobridged dirhodium compounds of general formula $[Rh_2(\mu\text{-Cl})(\mu\text{-PR}_2)L_4]$ [6] or $[Rh_2(\mu\text{-Cl})(\mu\text{-SR})L_4]$ [7]. The catalysts with one thiolato or phosphide bridge and one μ-Cl are active catalysts in hydrogenation, isomerization and hydroformylation, but the μ-Cl-bridged compounds decompose during such reactions.

We therefore decided to prepare mixed-bridged systems of the type $[M_2(\mu\text{-pz})(\mu\text{-PPh}_2)L_4]$ (M = Rh or Ir). The introduction of a pyrazolate into the bridged-phosphide systems may provide a more stable framework for homogeneous catalysis studies.

The present paper deals with the synthesis and characterization of dinuclear rhodium and iridium complexes containing an azolate group and a diphenylphosphide group as bridging ligands. An extension of this study to the preparation of heterotrinuclear compounds is also reported.

2. Results and discussion

We have recently reported a variety of heterobridged rhodium and iridium complexes containing pyrazolate-type ligands and a halogen or a terbutylthiolate group. The earlier preparation of $[M_2(\mu\text{-Cl})(\mu\text{-Pz})(COD)_2]$ (Pz = pyrazolate (pz) or 3,5-dimethylpyrazolate(dmpz); M = Rh or Ir)[4,8] or $[M_2(\mu\text{-Cl})(\mu\text{-PPh}_2)(COD)_2]$ (M = Rh or Ir)[9,10] suggested that the formation of mixed-bridged complexes containing the $[M_2(\mu\text{-az})(\mu\text{-PPh}_2)]$ (M = Rh or Ir; az = azolate) core might occur.

One of the synthetic routes, method 1, which led to these complexes has been a condensation of the appropriate mononuclear complexes followed by the substitution of the chloride bridge by a diphenylphosphide group, as indicated in the following equation:

$$[M(acac)(COD)] + [MCl(COD)(Haz)] \xrightarrow{-Hacac} [M_2(\mu\text{-Cl})(\mu\text{-az})(COD)_2] \xrightarrow[-LiCl]{+LiPPh_2} [M_2(\mu\text{-az})(\mu\text{-PPh}_2)(COD)_2]$$

M = Rh: az = pz (1), dmpz (2)
M = Ir: az = pz (3), dmpz (4)

(1)

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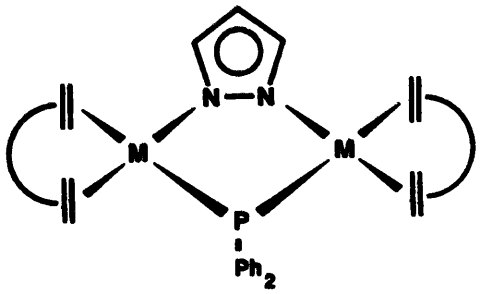
SSDI 0022-328X(95)05839-7



M = Rh, Ir

Fig. 1.

Complexes 1–4 have been fully characterized by analytical and spectroscopic data (see Section 3). In particular, the $^{31}P\{^1H\}$ spectra of the rhodium complexes show a triplet (50.55 ppm, $J_{RhP} = 114.0$ Hz (1); 67.99 ppm, $J_{RhP} = 107.5$ Hz (2)) corresponding to the phosphorus atom of the phosphide ligand which is coupled to two equivalent rhodium centres. These data indicate that the diphenylphosphide group is bridging (Fig. 1). As expected, the iridium compounds display a singlet in the $^{31}P\{^1H\}$ spectra (140.12 ppm (3); 139.06 ppm (4)).

An alternative route, method 2, for preparing the mixed-bridged rhodium complexes consists of the substitution of the chloride group of the dinuclear $[Rh_2(\mu\text{-}Cl)(\mu\text{-}PPh_2)(COD)_2]$ [10] by an azolate:

$$[Rh_2(\mu\text{-}Cl)(\mu\text{-}PPh_2)(COD)_2] + Liaz \longrightarrow [Rh_2(\mu\text{-}az)(\mu\text{-}PPh_2)(COD)_2]$$

az = pz(1), dmpz(2)

tz(5), ttz(6) (2)

In this case, the starting compound $[M_2(\mu\text{-}Cl)(\mu\text{-}PPh_2)(COD)_2]$ decomposes slowly in solution and is often contaminated with the double-phosphide-bridged complex $[M_2(\mu\text{-}PPh_2)_2(COD)_2]$. Consequently, although 1–4 were also prepared by this method, the yield was less than with method 1. However, this has been a very good method for isolating the dinuclear rhodium complexes $[Rh_2(\mu\text{-}tz)(\mu\text{-}PPh_2)(COD)_2]$ (5) (tz = triazolate) and $[Rh_2(\mu\text{-}ttz)(\mu\text{-}PPh_2)(COD)_2]$ (6) (ttz = tetrazolate). Method 1 is not useful in these cases because of the difficulty of preparing the mononuclear precursors [RhCl(COD)(Htz)] and [RhCl(COD)(Httz)].

Another method of preparation, method 3, consists of a conproportionation reaction of the double-azolate-bridged compound and the double-phosphide-bridged complex as shown in the following equation:

$$[Rh_2(\mu\text{-}az)_2(COD)_2] + [Rh_2(\mu\text{-}PPh_2)_2(COD)_2] \longrightarrow 2[Rh_2(\mu\text{-}az)(\mu\text{-}PPh_2)(COD)_2]$$

az = pz(1), tz(5) (3)

Compounds 1 and 5 have been prepared by this method but the yields are smaller than those obtained by methods 1 and 2.

An interesting area of research may be the controlled extension of the "$M(\mu\text{-}az)(\mu\text{-}PPh_2)M$" framework to form trinuclear systems of the type "$M(\mu\text{-}az)(\mu\text{-}PPh_2)M(\mu\text{-}az)(\mu\text{-}PPh_2)M$". An effective method of preparing well-defined heterotrinuclear systems has been recently described by our group, for the synthesis of the complexes $[\{M(\mu\text{-}pz)(\mu\text{-}L)(COD)\}_2Pd]$ (M = Rh or Ir; L = pz or S^{t}Bu) [11,12].

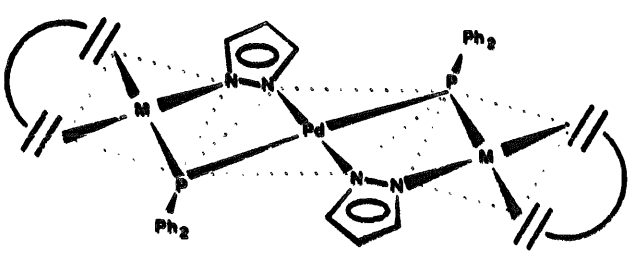
The reaction of $[\{Rh(\mu\text{-}Cl)(\mu\text{-}pz)(COD)\}_2Pd]$ (COD = cycloocta-1,5-diene), prepared in situ by linkage of the fragments [Rh(acac)(COD)] (acac = acetylacetonate) and $[PdCl_2(Hpz)_2]$, with $LiPPh_2$ affords the mixed-bridged trinuclear complex $[\{Rh(\mu\text{-}pz)(\mu\text{-}PPh_2)(COD)\}_2Pd]$ (7):

$$2[Rh(acac)(COD)] + [PdCl_2(Hpz)_2] \xrightarrow{-2Hacac} [\{Rh(\mu\text{-}Cl)(\mu\text{-}pz)(COD)\}_2Pd] \xrightarrow[-2LiCl]{2LiPPh_2} [\{Rh(\mu\text{-}pz)(\mu\text{-}PPh_2)(COD)_2\}_2Pd]$$

7 (4)

Compound 7 can exist as three geometrical isomers, but the $^{31}P\{^1H\}$ spectrum of the isolated complex shows the presence of one resonance (49.62 ppm) corresponding to two phosphide-bridges. The apparently simple resonance at 49.62 ppm appearing roughly as a doublet (142.6 Hz) is more complex and corresponds to the A portion of the AA'XX' system, composed of two P nuclei and two rhodium atoms. According to these data, only one of the possible isomers is present in solution. Considering the *trans* geometry present in the palladium complex $[PdCl_2(Hpz)_2]$ [11] and also the *trans*-bridge disposition observed for compounds $[\{M_2(\mu\text{-}pz)(\mu\text{-}S^tBu)(COD)\}_2Pd]$ (M = Rh or Ir) [12–14], we suggest that a *trans* configuration is also present in the trinuclear compound 7 (Fig. 2).

The synthetic route used for preparing 7 can be extended easily to the preparation of iridium complexes using [Ir(acac)(COD)] (acac = acetylacetonate) as pre-



M = Rh, Ir

Fig. 2.

cursor. The compound $[\{Ir(\mu\text{-}pz)(\mu\text{-}PPh_2)(COD)\}_2Pd]$ (8) isolated shows, as expected, only one singlet (143.84 ppm) in the $^{31}P\{^1H\}$ spectrum as a consequence of the equivalence of the phosphide bridges.

The present paper deals with the preparation of new heterobridged dinuclear and trinuclear complexes and shows the ability of azolates to form $M(\mu\text{-}az)(\mu\text{-}PPh_2)M$ five-membered rings.

3. Experimental part

All reactions were carried out under dinitrogen using standard Schlenk techniques, [Rh(acac)(COD)] [15], [Ir(acac)(COD)] [16], [RhCl(COD)(Hpz)] [17], [IrCl(COD)(Hpz)] [18], $[PdCl_2(Hpz)_2]$ [11], $[Rh_2(\mu\text{-}pz)_2(COD)_2]$ [19] and $[Rh_2(\mu\text{-}PPh_2)_2(COD)_2]$ [9] were prepared according to literature methods. Solvents were purified according to standard procedures and distilled under dinitrogen prior to use. All other reagents were purchased from Aldrich and used as received. Nujol mull IR spectra were recorded on a Nicolet Magna 550 spectrometer. ^1H and $^{31}P\{^1H\}$ NMR spectra were carried out in C_6D_6 and $CDCl_3$ solutions at room temperature on a Varian XL 300 spectrometer. ^{31}P chemical shifts are positive downfield from external 85% H_3PO_4 in D_2O. Elemental analyses were carried out on a Perkin–Elmer 240B microanalyser.

3.1. Preparation of $[Rh_2(\mu\text{-}pz)(\mu\text{-}PPh_2)(COD)_2]$ (1)

3.1.1. Method 1.

To a solution of $[Rh_2(\mu\text{-}Cl)(\mu\text{-}pz)(COD)_2]$ in tetrahydrofuran (THF) (20 ml) (prepared by reaction of [RhCl(COD)(Hpz)] (152 mg, 0.483 mmol) with [Rh(acac)(cod)] (150 mg, 0.483 mmol)) was added $LiPPh_2$ (0.483 mmol) in THF (5 ml) to give a red solution. After 24 h at room temperature the reaction afforded a yellow suspension. Then the suspension was evaporated to dryness and the residue extracted with dichloromethane (15 ml). Evaporation of the filtrate to dryness and addition of methanol (15 ml) gave a yellow solid which was filtered off, washed with cold methanol and vacuum dried (yield, 228 mg (70%)). ^1H NMR (C_6D_6): δ 1.81 (b, 8H, CH_2, COD), 2.22 (b, 8H, CH_2, COD), 3.82 (m, 4H, CH, COD), 4.81 (m, 4H, CH, COD), 6.05 (t, 1H, J_{HH} = 2.2 Hz, H^4, pz), 7.09 (d, 2H, J_{HH} = 2.2 Hz, $H^{3,5}$, pz), 7.33 (m, 8H, PPh_2), 7.95 (t, 2H, J_{HH} = 7.7 Hz, PPh_2) ppm. $^{31}P\{^1H\}$ NMR (C_6D_6 sol.): δ 50.55 (t, J_{RhP} = 114.0 Hz). Anal. Found: C, 55.10; H, 5.40; N, 4.25. $C_{31}H_{37}N_2PRh_2$ calc.: C, 55.21; H, 5.53; N, 4.15%.

3.1.2. Method 2.

Lithium pyrazolate (1 mmol), prepared in situ by reaction of $LiBu^n$ (1 mmol) and pyrazole (68 mg, 1 mmol), was added to a solution of $[Rh_2(\mu\text{-}Cl)(\mu\text{-}PPh_2)(COD)_2]$ in THF, prepared by reaction of $LiPPh_2$ (1 mmol) with $[Rh_2(\mu\text{-}Cl)_2(COD)_2]$] (493 mg, 1 mmol). The initial green solution became a yellow suspension after stirring for 36 h. Evaporation of the solvent and addition of toluene (10 ml) caused the complete precipitation of a yellow solid which was filtered off, washed with toluene and dried under vacuum. The isolated yellow solid was purified by addition of dichloromethane and filtering through kieselguhr. The yellow filtrate was then concentrated (1 ml) and addition of methanol gave a yellow compound which was separated by filtration and vacuum dried (yield, 337 mg (50%)).

3.1.3. Method 3.

The addition of $[Rh_2(\mu\text{-}pz)_2(COD)_2]$ (278.15 mg, 0.5 mmol) in acetone (15 ml), to a THF solution of $[Rh_2(\mu\text{-}PPh_2)_2(COD)_2]$ (396 mg, 0.5 mmol) caused the formation of a green suspension which changed to yellow after stirring for 48 h. Concentration of the solvent to dryness and addition of diethyl ether (10 ml) gave a yellow solid which was separated by filtration, washed with diethyl ether and vacuum dried (yield, 101 mg (30%)).

3.2. Preparation of $[Rh_2(\mu\text{-}dmpz)(\mu\text{-}PPh_2)(COD)_2]$ (2)

Compound 2 was prepared by methods 1 and 2 described for compound 1 starting from [RhCl(COD)(Hdmpz)] (167.45 mg, 0.483 mmol), [Rh(acac)(COD)] (150 mg, 0.483 mmol) and $LiPPh_2$ (0.483 mmol) (yield, 271 mg (80%)) for method 1, and starting from $[Rh_2(\mu\text{-}Cl)(\mu\text{-}PPh_2)(COD)_2]$ (321.36 mg, 0.5 mmol) and Lidmpz (0.5 mmol) (yield, 211 mg (60%)) for method 2. ^1H NMR (C_6D_6 sol.): δ 2.04 (s, 6H, Me, dmpz), 2.21 (s, 8H, CH_2, COD), 2.40 (s, 8H, CH_2, COD), 3.55 (b, 4H, CH, COD), 3.80 (b, 4H, CH, COD) 6.90 (b, 1H, H^4 dmpz), 7.10 (m, 8H, PPh_2), 7.95 (b, 2H, PPh_2) ppm. $^{31}P\{^1H\}$ NMR (C_6D_6 sol.): δ 67.99 (t, J_{Rh-P} = 107.5 Hz) ppm. Anal. Found: C, 56.21; H, 5.40; N, 3.68. $C_{33}H_{41}N_2PRh_2$ calc.: C, 56.42; H, 5.88; N, 3.98%.

3.3. Preparation of $[Ir_2(\mu\text{-}Pz)(\mu\text{-}PPh_2)(COD)_2]$ (Pz = pz (3) on dmpz (4))

Compounds 3 and 4 were prepared by method 1 described for 1 using as starting materials [Ir(acac)(COD)] (150 mg, 0.375 mol), [IrCl(COD)(HPz)] (HPz = Hpz (152 mg, 0.375 mmol), Hdpmz (162 mg, 0.375 mmol)) and $LiPPh_2$ (0.375 mmol). The reaction time for 3 and 4 was 2 h. The yield of 3 (orange) was 178 mg, (67%). Anal. Found: C, 43.59; H, 4.35; N, 3.1. $C_{31}H_{37}Ir_2N_2P$ calc.: C, 43.64; H, 4.37; N, 3.28%. $^{31}P\{^1H\}$ NMR (C_6D_6 sol.): δ 140.12 (s) ppm. The yield of 4 (violet): was 264 mg (80%). Anal. Found: C,

44.55; H, 4.48; N, 3.02. $C_{33}H_{41}Ir_2N_2P$ calc.: C, 44.98; H, 4.69; N, 3.18%. $^{31}P\{^1H\}$NMR($CDCl_3$ sol.): δ 139.06 (s) ppm.

3.4. Preparation of $[Rh_2(\mu\text{-}tz)(\mu\text{-}PPh_2)(COD)_2]$ (5)

Compound **5** was prepared by methods 2 and 3 described for **1** starting from $[Rh_2(\mu\text{-}Cl)(\mu\text{-}PPh_2)(COD)_2]$ (321.36 mg, 0.5 mmol) and $(NHEt_3)tz$ (0.5 mmol) (yield, 202 mg (60%); reaction time, 12 h (method 2); colour, yellow), and starting from $[Rh_2(\mu\text{-}tz)_2(COD)_2]$ (139 mg, 0.25 mmol) and $[Rh_2(\mu\text{-}PPh_2)_2(COD)_2]$ (198 mg, 0.25 mmol) (yield, 51 mg (30%); reaction time, 12 h (method 3); colour, yellow). ^1H NMR (C_6D_6 sol.): δ 2.02 (b, 8H, CH_2, COD), 2.54 (b, 8H, CH_2, COD), 3.80 (b, 4H, CH, COD), 4.50 (b, 4H, CH, COD), 6.90 (m, 10H, pz, PPh_2), 7.80 (t, 2H, J_{HH} = 8.4 Hz, PPh_2). $^{31}P\{^1H\}$ NMR (C_6D_6 sol.): δ 48.28 (t, J_{RhP} = 114.4 Hz) ppm. Anal. Found: C, 52.91; H, 5.23; N, 6.19. $C_{30}H_{36}N_3PRh_2$ calc.: C, 53.34; H, 5.37; N, 6.22%.

3.5. Preparation of $[Rh_2(\mu\text{-}ttz)(\mu\text{-}PPh_2)(COD)_2]$ (6)

Compound **6** was prepared by method 2 described for **1** starting from $[Rh_2(\mu\text{-}Cl)(\mu\text{-}PPh_2)(COD)_2]$ (321.36 mg, 0.5 mmol) and $(NHEt_3)ttz$ (0.5 mmol) (yield, 220 mg, (65%); reaction time, 12 h; colour, yellow). ^1H NMR (C_6D_6 sol.): δ 2.10 (m, 8H, CH_2, COD), 2.62 (m, 8H, CH_2, COD), 4.01 (m, 4H, CH, COD), 4.52 (m, 4H, CH, COD), 7.10 (m, 9H, ttz, PPh_2), 7.95 (t, 2H, J_{HH} = 7.9, PPh_2) ppm. $^{31}P\{^1H\}$ NMR (C_6D_6 sol.): δ 45.69 (t, J_{RhP} = 113.3 Hz) ppm. Anal. Found: C, 50.8; H, 5.26; N, 8.12. $C_{30}H_{35}N_4PRh_2$ calc.: C, 51.29; H, 5.56; N, 8.25%.

3.6. Preparation of $[\{Rh(\mu\text{-}pz)(\mu\text{-}PPh_2)(COD)\}_2Pd]$ (7)

To a solution of $[\{Rh(\mu\text{-}Cl)(\mu\text{-}pz)(COD)\}_2Pd]$ (prepared in situ by reaction of [Rh(acac)(COD)] (200 mg, 0.64 mmol) with $[PdCl_2(Hpz)_2]$ (101 mg, 0.32 mmol) in THF (20 ml) was added $LiPPh_2$ (0.64 mmol) in diethyl ether. The resulting red suspension was stirred for 48 h at room temperature. The evaporation of the solvents and addition of methanol (5 ml) gave a brown–red solid which was separated by filtration, washed with methanol and vacuum dried (281 mg (85%)). ^1H NMR ($CDCl_3$ sol.): δ 2.35 (b, 8H, CH_2, COD), 3.45 (b, 8H, CH_2, COD), 4.10 (b, 4H, CH, COD), 4.35 (b, 4H, CH, COD), 6.51 (t, 2H, J_{HH} = 2.2 Hz, H^4, pz), 7.32 (m, 24H, pz, PPh_2) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$ sol.): δ 49.62 ($^1J_{RhP} + {}^xJ_{RhP}$ = 142.6 Hz) ppm. Anal. Found: C, 53.21; H, 4.61; N, 5.27. $C_{46}H_{50}N_4P_2PdRh_2$ calc.: C, 53.47; H, 4.87; N, 5.42%.

3.7. Preparation of $[\{Ir(\mu\text{-}pz)(\mu\text{-}PPh_2)(COD)\}_2Pd]$ (8)

Compound **8** was prepared by the method described for **7** starting from [Ir(acac)(COD)] (99.8 mg, 0.25 mmol), $[PdCl_2(Hpz)_2]$ (39.2 mg, 0.125 mmol), $LiPPh_2$ (0.25 mmol). (yield, 106 mg (70%); reaction time, 6 h; colour, orange) ^1H NMR ($CDCl_3$ sol.): δ 2.21 (b, 8H, CH_2, COD), 2.75 (b, 8H, CH_2, COD) 3.50 (b, 4H, CH, COD), 3.85 (b, 4H, CH, COD), 6.51 (t, 2H, J_{HH} = 2.2 Hz, H^4 pz), 7.25 (m, 24H, pz, PPh_2) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$ solid): 143.84 (s) ppm. Anal. Found: C, 45.20; H, 4.13; N, 4.47. $C_{46}H_{50}Ir_2N_4P_2Pd$ calc.: C, 45.59; H, 4.16; N, 4.62%.

Acknowledgements

We thank the Dirección General de Investigación Científica y Técnica for financial support (PB92-0086) and also the Consejo Superior de Investigaciones Científicas (CSIC) for a grant to support the stay of E.B. at the Universidad de Zaragoza under the CSIC–Hebrew University cooperation agreement. We also thank Nuria Navarro for her initial help.

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