Inorganica Chimica Acta, *169* (1990) 39–42

Synthesis and Characterisation of Binuclear Phosphite Complexes of Rhodium(I) with Bridging Azines*

SARADA GOPINATHAN, SANJEEVANI A. PARDHY, I. R. UNNY and C. GOPINATHAN**

Inorganic Chemistry Division, National Chemical Laboratory, Pune 411 008 (India)

(Received June 16, 1989)

Abstract

Carbonyl ligand substitution in binuclear rhodium(I) complexes such as $[Rh(CO)_2]_2$(azine) with trialkyl or triphenyl phosphite gave mono- and di-substituted phosphite derivatives, $\{Rh(CO)[P(OR)_3]\}_2$(azine) and $\{Rh[P(OR)_3]_2\}_2$(azine). The complexes have been characterised by elemental analysis, IR and NMR studies. The ^1H and ^{31}P NMR spectra of the mono-substituted unsymmetrical azine complex $\{Rh(CO)[P(OMe)_3]\}_2$(Salba-az) show the presence of two non-equivalent phosphorus nuclei.

Introduction

It is well known that triphenylphosphine substitutes only one carbonyl group in mononuclear rhodium(I) complexes of the type $Rh(CO)_2(L\text{-}L')$, where L-L′ is a monobasic bidentate chelating ligand like β-diketones [1, 2], tropolone [3] and 8-hydroxyquinoline [4]. The *trans* influence of the bonded atoms in the bidentate ligands has been established by this substitution reaction. So far only a few mononuclear, square planar rhodium(I) complexes with trialkyl/aryl phosphites have been investigated [5, 6]. Trzeciak and Ziolkowski [7] have substituted both the carbonyl groups in the mononuclear complex $[Rh(CO)_2(acac)]$ by triphenyl phosphite under mild conditions. There is no mention in the literature about substitution reactions involving binuclear rhodium(I) carbonyl complexes and organic phosphites. In continuation of our work on binuclear rhodium(I) carbonyl complexes of aromatic azines [8], we report herein the mono- and di-substitution of carbonyl ligand using trialkyl and triphenyl phosphites.

Experimental

Reactions were carried out in an atmosphere of pure, dry nitrogen. The reagents used were of highest available purity. Methanol was dried over magnesium turnings and freshly distilled. Petroleum ether (40–60°) fraction) was dried over sodium wire and distilled. Trimethyl, triisopropyl and triphenyl phosphites (Aldrich or Fluka) were used as such without further purification. Tetracarbonyldichlorodirhodium $[Rh(CO)_2Cl]_2$ [9] and tetracarbonyldirhodium azine $[Rh(CO)_2]_2$(azine) [8] were prepared by methods mentioned in the literature.

The IR spectra were recorded on a Perkin-Elmer Model 599 IR spectrophotometer using Nujol mulls, KBr pellets or chloroform solutions. ^1H NMR spectra were measured on a Bruker 90 spectrometer.

Two typical procedures for the isolation of substitution reaction products are illustrated below. Abbreviations are indicated in Table 1.

Preparation of Salicylaldazinodirhodiumtetratrimethyl Phosphite, $\{Rh[P(OMe)_3]_2\}_2$(Sal-az)

To the complex $[Rh(CO)_2]_2$(Sal-az) (0.55 g; 1 mmol), an excess of trimethyl phosphite (0.58 g; 48 mmol) was added. The gas evolution was noted and the orange yellow solid which separated was collected by filtration, washed with methanol and then with petroleum ether (40–60°) and dried *in vacuo* at 30 °C. The product weighed 0.65 g (70% of theory). Melting point (m.p.) 204 °C (d).

Preparation of Salicylaldehyde-benzoylacetone–azinodicarbonyldirhodiumbis-trimethylphosphite $\{Rh(CO)[P(OMe)_3]\}_2$(Salba-az)

$[Rh(CO)_2]_2$(Salba-az) (0.596 g; 1 mmol) and trimethyl phosphite (0.27 g; 22 mmol) were mixed in methanol (30 ml) and stirred at ambient temperature for 24 h. The brown solid which separated was filtered, washed with petroleum ether and dried *in vacuo*. Yield 0.63 g (80% of theory). M.p. 270 °C (d).

Results and Discussion

The binuclear complex $[Rh(CO)_2]_2$(azine) reacts with an excess of trialkyl/aryl phosphites to yield the carbonyl free disubstitution product

---

*NCL Communication No. 4329.

**Author to whom correspondence should be addressed.

0020-1693/90/$3.50

TABLE 1. Analytical data of binuclear phosphite complexes with bridging azines

Compound no.	Compound/Empirical formula[a]	Melting/ decomposition temperature (°C)	Yield (%)	Analysis: found (calc.) (%)			
				C	H	N	P
1	$\{Rh[P(OC_6H_5)_3]_2\}_2$(Sal-az)	263	60	61.16	4.01	1.57	7.67
	$Rh_2C_{86}H_{70}N_2O_{14}P_4$			(61.28)	(4.15)	(1.06)	(7.36)
2	$\{Rh[P(OCH_3)_3]_2\}_2$(Sal-az)	204	70	30.85	4.66	2.90	12.03
	$Rh_2C_{26}H_{46}N_2O_{14}P_4$			(30.00)	(4.42)	(2.69)	(11.92)
3	$\{Rh[P(OC_3H_7)_3]_2\}_2$(Sal-az)	220	75	47.18	7.57	2.82	9.52
	$Rh_2C_{50}H_{94}N_2O_{14}P_4$			(47.02)	(7.36)	(2.19)	(9.71)
4	$\{Rh[P(OC_6H_5)_3]_2\}_2$(Acph-az)	195	65	61.82	4.44	1.82	7.57
	$Rh_2C_{88}H_{74}N_2O_{14}P_4$			(61.60)	(4.32)	(1.63)	(7.24)
5	$\{Rh[P(OCH_3)_3]_2\}_2$(Acph-az)	260	60	34.54	5.36	2.22	12.32
	$Rh_2C_{28}H_{50}N_2O_{14}P_4$			(34.78)	(5.16)	(2.89)	(12.81)
6	$\{Rh[P(OC_3H_7)_3]_2\}_2$(Acph-az)	255	67	47.66	7.18	2.90	9.17
	$Rh_2C_{52}H_{98}N_2O_{14}P_4$			(47.85)	(7.51)	(2.14)	(9.51)
7	$\{Rh[P(OC_6H_5)_3]_2\}_2$(Salba-az)	212	72	61.84	4.55	1.33	7.33
	$Rh_2C_{89}H_{74}N_2O_{14}P_4$			(61.98)	(4.29)	(1.62)	(7.19)
8	$\{Rh[P(OCH_3)_3]_2\}_2$(Salba-az)	237	68	35.72	5.43	2.66	12.37
	$Rh_2C_{29}H_{50}N_2O_{14}P_4$			(35.51)	(5.10)	(2.85)	(12.65)
9	$\{Rh[P(OC_3H_7)_3]_2\}_2$(Salba-az)	290	63	48.56	7.67	2.45	9.17
	$Rh_2C_{53}H_{98}N_2O_{14}P_4$			(48.32)	(7.44)	(2.12)	(9.42)
10	$\{Rh[P(OC_6H_5)_3]_2\}_2$(Salacph-az)	286	65	61.34	4.52	1.82	7.76
	$Rh_2C_{87}H_{72}N_2O_{14}P_4$			(61.55)	(4.24)	(1.65)	(7.31)
11	$\{Rh[P(OCH_3)_3]_2\}_2$(Salacph-az)	270	67	33.80	5.27	2.62	12.72
	$Rh_2C_{27}H_{48}N_2O_{14}P_4$			(33.96)	(5.03)	(2.93)	(12.99)
12	$\{Rh[P(OC_3H_7)_3]_2\}_2$(Salacph-az)	258	68	47.65	7.62	2.22	9.45
	$Rh_2C_{51}H_{96}N_2O_{14}P_4$			(47.64)	(7.44)	(2.17)	(9.61)
13	$\{Rh(CO)[P(OCH_3)_3]\}_2$(Sal-az)	257	70	35.42	3.51	3.91	8.45
	$Rh_2C_{22}H_{28}N_2O_{10}P_2$			(35.29)	(3.74)	(3.74)	(8.28)
14	$\{Rh(CO)[P(OCH_3)_3]\}_2$(Acph-az)	266	75	37.56	4.32	3.53	8.33
	$Rh_2C_{24}H_{30}N_2O_{10}P_2$			(37.79)	(4.19)	(3.67)	(8.13)
15	$\{Rh(CO)[P(OCH_3)_3]\}_2$(Salba-az)	270	80	38.27	4.44	3.42	7.72
	$Rh_2C_{25}H_{32}N_2O_{10}P_2$			(38.07)	(4.06)	(3.55)	(7.86)
16	$\{Rh(CO)[P(OC_3H_7)_3]\}_2$(Salacph-az)	277	65	45.41	5.68	3.22	6.47
	$Rh_2C_{35}H_{54}N_2O_{10}P_2$			(45.16)	(5.80)	(3.01)	(6.66)

[a] Abbreviations: (Sal-az)H_2 = salicylaldazine, (Acph-az)H_2 = 2-hydroxyacetophenone azine, (Salba-az)H_2 = salicylaldehyde benzoylacetone azine, (Salacph-az)H_2 = salicylaldehyde 2-hydroxyacetophenone azine.

$\{Rh[P(OR)_3]_2\}_2$(azine) (**I**) with rapid liberation of carbon monoxide gas.

$$[Rh(CO)_2]_2(\text{azine}) + 4P(OR)_3 \longrightarrow \{Rh[P(OR)_3]_2\}_2(\text{azine}) + 4CO$$

The products are yellow to orange solids melting above 200 °C and soluble in common organic solvents. Mono-substitution products of the type $\{Rh(CO)[P(OR)_3]_2\}_2$(azine) (**II**) are also obtained using a 1:1 stoichiometric quantity of the reactants in methanol.

$$[Rh(CO)_2]_2(\text{azine}) + 2P(OR)_3 \longrightarrow [Rh(CO)P(OR)_3]_2(\text{azine}) + 2CO$$

The new rhodium compounds synthesised are reported in Table 1. These brown solids melt with decomposition above 200 °C and are sparingly soluble in common solvents.

The IR spectra (Table 2) of the di-substituted products [I] show complete absence of carbonyl bands ~2000 cm^{-1}. The ν(C=N) in the azine derivatives is seen at 1600 cm^{-1}. The ν(N–N) has been

TABLE 2. IR (ν, cm^{-1}) and ^{1}H NMR (chemical shift, δ ppm) spectral data for binuclear rhodium(I) phosphite complexes with bridging azines

Compound no.[a]	(C≡O)	(C=N)	(C–O)	(P–O–C)	(N–N)	CH_3	OCH_3	CH	Aromatic protons	Aldehydic CH
1		1600	1305	1215	920					
2		1600	1310	1030	930		3.7d		7.0 - 7.5	8.4
3		1600	1310	1030	930	1.3m		4.6m	7.4	8.4
4		1600	1320	1220	975	2.6s			6.7 - 7.8	
5		1600	1320	1010	980	2.6s	3.8d		6.4 - 7.8	
6		1600	1320	950	975	1.35q 2.6s		4.6m	6.8 - 7.8	
7		1600	1315	1220	920	2.4s		5.8s	6.2 - 8.0	8.4
8		1600	1310	1020	930	2.4s	3.8d	5.8s	6.6 - 7.5	8.5
9		1600	1310	990	925	1.3m 2.4s		4.6m 5.7s	6.3 - 8.2	8.5
10		1600	1310	1220	930	2.6s			6.2 - 8.1	8.4
11		1600	1310	1000	930	2.6s	3.8d		6.3 - 7.9	8.5
12		1600	1310	985	930	1.3m 2.4s		4.4m	6.7 - 7.5	8.4
13	1960, 1970 1995	1595	1310	1010	910		3.8d		6.5 - 7.5	8.7 8.9
14	1960, 1970 2000	1595	1330	1015	925	2.6s	3.8d		6.4 - 7.8	
15	1965, 1980 2000	1600	1320	1030	930	2.4s	3.7d	5.7	6.5 - 8.5	8.3 8.4
16	1965, 1980 2000	1600	1310	980	930	1.4d 2.6s		4.6	6.6 - 7.8	8.6

[a]See Table 1 for formulae.

shifted to lower frequency as compared to the starting dicarbonyl derivatives. In the case of mononuclear group IV metal complexes of azines splitting of ν(C=N) and ν(N–N) due to dissimilar ring formation is a common phenomenon [10]; but there is no splitting with rhodium azine complexes which suggests that the lone pairs on both nitrogens coordinate to their respective rhodium atoms. The ν(P–O–C) is observed at ~1220 and ~1015 cm^{-1} in the cases of triphenyl and trialkyl phosphites respectively.

In the ^{1}H NMR spectra the azomethine >CH and CH_3 protons of the salazine and acetophenone azine rhodium(I) phosphite complexes resonate at higher magnetic field compared to the respective binuclear rhodium carbonyl complexes [8]. This upfield shift can be explained due to the presence of alkyl phosphites, which being strong σ donors and poor π acids, increase the electron density at the rhodium atoms by coordination with the lone pair on phosphorus in place of carbon monoxide.

The trimethyl phosphite complexes 2, 5 and 8 show OCH_3 resonance at ~3.8 ppm (OCH_3 in $P(OCH_3)_3 = \delta$ 3.55 d) as a doublet with $^3J(PH) =$ ~10 Hz (Fig. 1). In the isopropyl phosphite derivative $\{Rh[P(OC_3H_7{}^i)_3]_2\}_2$(Acph-az) (compound **6**) the methyl protons resonate as a doublet centered at ~1.35 ppm with a coupling constant of $^4J(PH) =$ 6.3 Hz and the methine proton CH absorbs at 4.7 as a multiplet. The downfield shift of CH_3 and >CH resonances in the above complexes compared to the free isopropyl phosphite ligand at δ 1.25 d and 4.45 m respectively is attributed to the strong σ donation of the lone pair on phosphorus to rhodium. The above data suggest a square planar geometry for both the rhodium atoms in the disubstituted complexes as shown in Fig. 2.

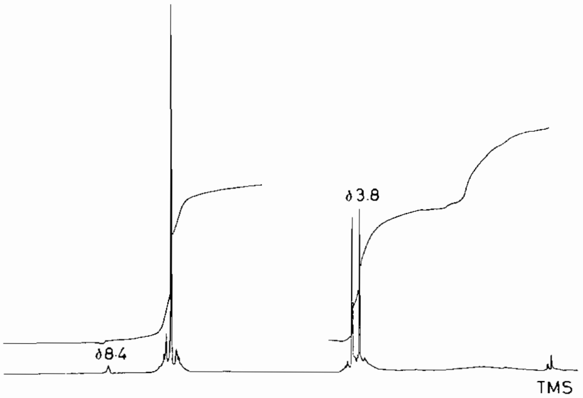

Fig. 1. NMR spectrum of $\{Rh[P(OMe)_3]_2\}_2$(Sal-az).

The IR spectra of mono-substituted complexes in Nujol mulls exhibit more than one absorption band between 1960–2000 cm^{-1} due to ν(C≡O). The

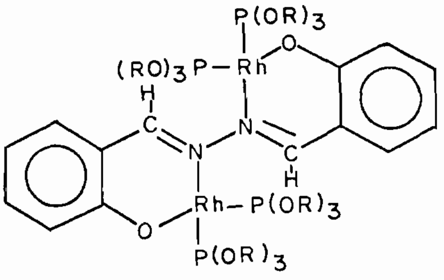

Fig. 2. $\{Rh[P(OR)_3]_2\}_2$(Sal-az).

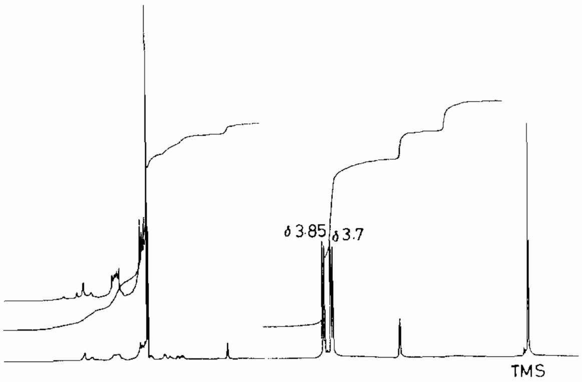

Fig. 3. NMR spectrum of $\{Rh(CO)[P(OMe)_3]\}_2$(Salba-az).

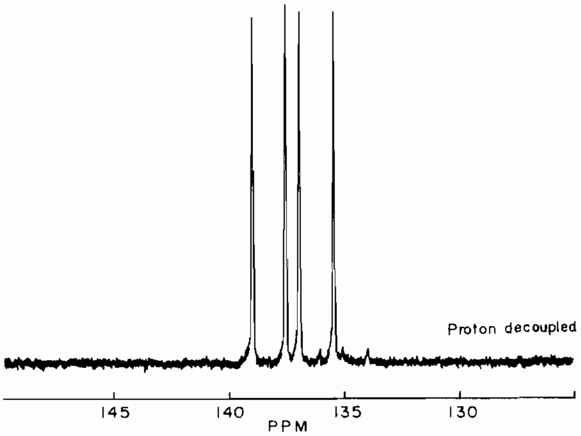

Fig. 4. ^{31}P NMR spectrum of $\{Rh(CO)[P(OMe)_3]\}_2$(Salba-az).

solution spectra of these complexes in chloroform show only a single absorption at 1990 cm^{-1}, indicating that solid state interactions result in a splitting of the CO stretching bands. The ^1H NMR spectrum of the trimethyl phosphite complex $\{Rh(CO)[P(OCH_3)_3]\}_2$(Salba-az) exhibits two doublets due to OCH_3 protons at δ 3.70 and 3.85 ppm with $^3J(PH) \sim$ 8 Hz (Fig. 3). The ^{31}P NMR spectrum (Fig. 4) shows two doublets at δ 138.22 and 136.15 ppm due to the presence of two non-equivalent phosphorus nuclei with $^1J(Rh-P_1) = 175$ and $^1J(Rh-P_2) = 185$ Hz respectively. The non-equivalent nature of the phosphorus nuclei would probably arise from the bridging of two rhodium atoms with an unsymmetrical azine molecule in a square planar environment as shown in Fig. 5. Because of limited solubility, the ^{31}P NMR spectra of remaining compounds could not be taken.

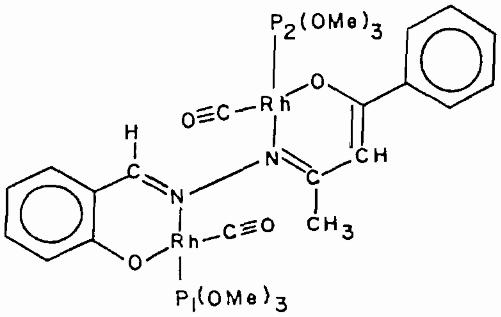

Fig. 5. $\{Rh(CO)[P(OMe)_3]\}_2$Salba-az.

References

1 J. G. Leipoldt, S. S. Basson, L. D. C. Bok and T. I. A. Gerber, *Inorg. Chim. Acta, 26* (1978) L35.
2 J. G. Leipoldt, L. D. C. Bok, J. S. Van Vollenhoven and A. I. Pieterse, *J. Inorg. Nucl. Chem., 40* (1978) 61.
3 J. G. Leipoldt, L. D. C. Bok, S. S. Basson and H. Meyer, *Inorg. Chim. Acta, 42* (1980) 105.
4 J. G. Leipoldt, S. S. Basson and C. R. Dennis, *Inorg. Chim. Acta, 50* (1981) 121.
5 V. W. Day, M. F. Fredrick, G. S. Reddy, A. J. Swak, W. R. Pretzer and E. L. Muetterties, *J. Am. Chem. Soc., 99* (1977) 8091.
6 P. Meakin and J. P. Jesson, *J. Am. Chem. Soc., 96* (1974) 5751.
7 A. M. Trzeciak and J. J. Ziolkowski, *Inorg. Chim. Acta Lett., 64* (1982) L267.
8 S. Gopinathan, S. A. Pardhy, C. Gopinathan, V. G. Puranik, S. S. Tavale and T. N. Guru Row, *Inorg. Chim. Acta, 111* (1986) 133.
9 J. A. McCleverty and G. Wilkinson, *Inorg. Synth., 10* (1966) 211.
10 S. Gopinathan, H. A. Patwardhan and C. Gopinathan, *Indian J. Chem., 16A* (1978) 224.