ELSEVIER

www.elsevier.nl/locate/jorganchem

Journal of Organometallic Chemistry 599 (2000) 313–316

Journal of Organo metallic Chemistry

Note

# The reaction of $[Ru_3(CO)_{12}]$ with bis(diphenylphosphino)amine. The crystal and molecular structure of $[Ru_3(CO)_{10}(dppa)]$ and $[Ru_3(CO)_8(dppa)_2]$

Gloria Sánchez-Cabrera, Efrén V. García-Báez, María J. Rosales-Hoz *

*Departamento de Química, Centro de Investigación y de Estudios Avanzados del IPN, AP 14-740, DF 07000, Mexico, Mexico*

Received 29 October 1999; received in revised form 15 December 1999

**Abstract**

The reaction of $[Ru_3(CO)_{12}]$ with bis(diphenylphosphino)amine (dppa) in the presence of sodium benzophenone leads to $[Ru_3(CO)_{10}(dppa)]$ in quantitative yield, while the same reaction carried out in refluxing toluene also produces the disubstituted product $[Ru_3(CO)_8(dppa)_2]$. Both products were characterized spectroscopically and by X-ray crystallography. The five-membered rings, formed by the coordinated ligand and the two metal atoms, show distorted envelope conformations. There are significant differences in the P–N bond lengths of each dppa ligand in the disubstituted cluster while they are totally symmetric in the monosubstituted derivative. © 2000 Elsevier Science S.A. All rights reserved.

*Keywords:* Bis(diphenylphosphino)amine; Ruthenium cluster; X-ray structure

## 1. Introduction

The coordination chemistry of bis(diphenylphosphino)amine (dppa), $Ph_2PN(H)PPh_2$, has attracted the attention of some research groups [1] interested in the spectroscopic and physical properties of complexes containing this ligand, similar to the more studied bis(-diphenylphosphibo)methane (dppm). This is partly due to the fact that some theoretical studies [2] suggested a greater ring strain in dppa derivatives than in the corresponding dppm ones. This strain should be less important when dppa coordinates to two metal centers, but then a different electronic distribution in the polynuclear compound might be expected. In addition, the greater acidity of the NH proton may also induce other reactions.

As far as we are aware, not many dppa-substituted carbonyl clusters have been prepared. Moodley and co-workers [3] reported the synthesis of $[Ru_3(CO)_{10}(\mu\text{-}Ph_2PN(Et)PPh_2)]$, containing a related ligand, prepared by photochemical activation of $[Ru_3(CO)_{12}]$. $CoPd_2$ and $Pd_4$ complexes of dppa and other related ligands have also been described [4,5].

As part of a study of the reactivity of diphosphine-substituted clusters, we have prepared and characterized spectroscopically and by X-ray crystallography, the dppa mono- and disubstituted derivatives of $[Ru_3(CO)_{12}]$. The results of these experiments are reported herein.

## 2. Results and discussion

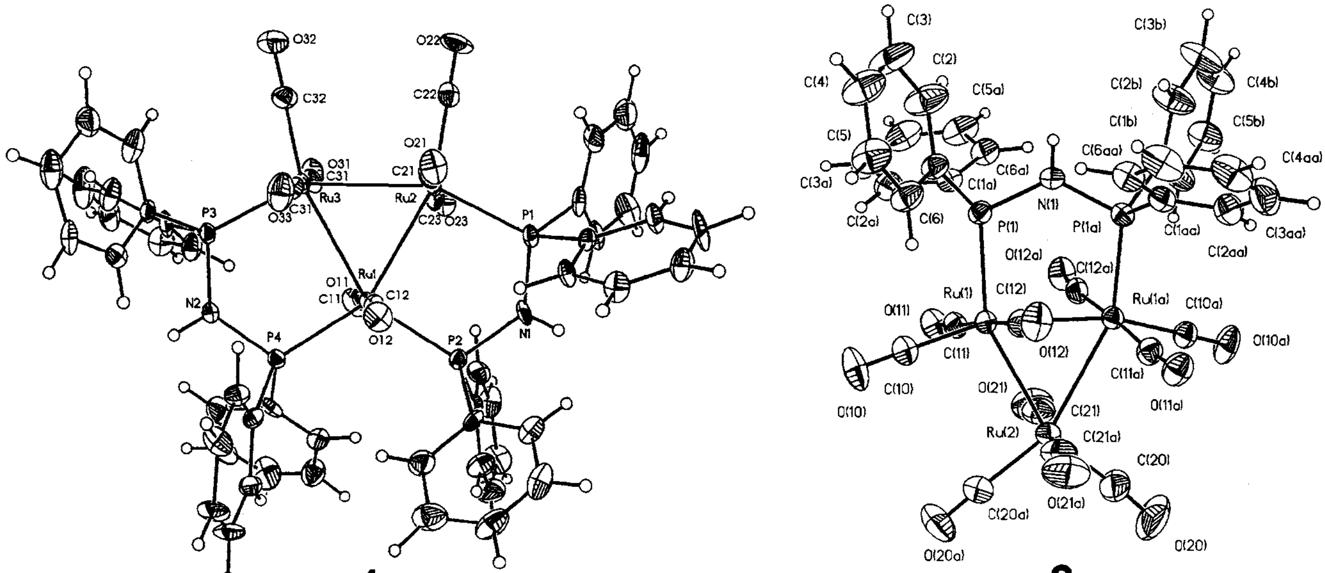
The reaction of $[Ru_3(CO)_{12}]$ with one equivalent of dppa in refluxing toluene, yields two products in 60% (**1**) and 30% (**2**) yields. Some ruthenium carbonyl is also recovered.

---

* Corresponding author: Fax: + 52-57-477113.

*E-mail address:* mrosales@mail.cinvestav.mx (M.J. Rosales-Hoz)

PII: S0022-328X(99)00767-6



**1** **2**

Fig. 1. Molecular structure of $[Ru_3(CO)_8(dppa)_2]$ (**1**) and of $[Ru_3(CO)_{10}(dppa)]$ (**2**).

Product **1** is red with an infrared spectrum showing carbonyl stretching frequencies[1] similar to those observed in $[Ru_3(CO)_8(dppm)_2]$ [6]. Proton NMR spectroscopy shows two triplets of equal intensity that suggest two different NH groups. Both signals are shifted to lower fields than those of the free ligand (3.8 ppm). The $^{31}P$-NMR spectrum of **1** consists of an AA′XX′ spin system centered in 69.66 ppm. The spectroscopic evidence suggests **1** to be $[Ru_3(CO)_8(dppa)_2]$.

Compound **2** shows an infrared spectrum similar to that of $[Ru_3(CO)_{10}(dppm)]$ [7] in the carbonyl region. The proton NMR shows a triplet in 4.7 ppm also thought to be due to a NH proton and is shifted to an even lower field than those in **1**. The $^{31}P$-NMR shows a singlet ($\delta$ 69.6 ppm) shifted to a higher frequency than the one in the free ligand ($\delta$ 42.5 ppm). Thus, compound **2** is proposed to have the formulation $[Ru_3(CO)_{10}(dppa)]$.

Comparing the spectroscopic data of both compounds, we can appreciate that the $^2J$(P–H) constant is higher in **1** than in **2** but lower than in the free ligand. That of **2** is also lower than the corresponding value in free dppa. This might be an indication of a higher electron density in the P–N–H fragment in **1** than in **2** but lower in both **1** and **2** than in the free ligand.

Table 1
Selected bond lengths (Å) and angles (°) for **1** and **2**

| | **1** | **2** |
|---|---|---|
| *Bond lengths* | | |
| Ru(1)–Ru(2) | 2.823(2) | 2.8546(10) |
| Ru(1)–Ru(3) | 2.833(3) | |
| Ru(2)–Ru(3) | 2.8223(13) | |
| Ru(1)–Ru(1a) | | 2.8287(11) |
| Ru(2)–Ru(1a) | | 2.8545(10) |
| Ru(1)–P(2) | 2.304(3) | |
| Ru(2)–P(1) | 2.303(3) | |
| Ru(1)–P(4) | 2.292(3) | |
| Ru(3)–P(3) | 2.293(3) | |
| Ru(1)–P(1) | | 2.307(2) |
| P(1)–N(1) | 1.660(10) | 1.688(4) |
| P(2)–N(1) | 1.728(9) | |
| P(3)–N(2) | 1.674(10) | |
| P(4)–N(2) | 1.724(9) | |
| *Bond angles* | | |
| P(1)–N(1)–P(2) | 127.6(6) | |
| P(3)–N(2)–P(4) | 126.2(6) | |
| P(1)–N(1)–P(1a) | | 127.1(5) |

---

[1] Compound **1**. $[Ru_3(CO)_8(dppa)_2]$ was prepared by reaction of 0.1 g of $[Ru_3(CO)_{12}]$ (0.1564 mmol) and 0.0580 g of $(PPh_2)_2NH$ (0.15 mmol) in 50 ml of toluene heated to reflux for 2 h. The reaction mixture was dried under vacuum and the residue separated on a chromatographic column using 60:30:10: hexane–acetone–$CH_2Cl_2$ as eluent. Some $[Ru_3(CO)_{12}]$ was recovered together with compound **1** (60% yield). After changing the eluent to $CHCl_3$ an additional compound was separated and identified as $[Ru_3(CO)_{10}(dppa)]$ (**2**) (30% yield). Compound **1**, $\nu$(CO) ($CH_2Cl_2$) $cm^{-1}$: 2045 (s), 1974 (sh), 1910 (w). $^1H$-NMR (ppm) [$^2J$(H–P) (Hz)]: 7.04–7.19 (m), 4.04 (t) [6.08], 3.98 (t) [5.98]. $^{31}P$-NMR (ppm) 69.66 (AA′XX′). Compound **2**. $\nu$(CO) ($CH_2Cl_2$) ($cm^{-1}$) 2082 (m), 2014 (vs), 2000 (s), 1979 (sh), 1961 (m). $^1H$-NMR (ppm) [$^2J$(H–P) (Hz)]: 7.40–7.20 (m), 4.7 (t) [4.9]. $^{31}P$-NMR (ppm): 65.6. $[Ru_3(CO)_{10}(dppa)]$ (**2**) can also be prepared by the use of Bruce's catalyst [13]. $[Ru_3(CO)_{12}]$ (0.050 g) was dissolved in 10 ml of THF and 5–6 drops of $Ph_2CO^-$ were added and finally 0.0303 g of $(PPh_2)_2NH$ was also added to the solution. An immediate change of color was observed and after addition of some 8 to 10 more drops of catalyst, the mixture was stirred at room temperature for 5 min. The solution was then concentrated and crystals, suitable for X-ray diffraction study, were obtained from a chloroform solution.

Crystals of both **1** and **2** were studied by X-ray diffraction[2] and the results are shown in Fig. 1. Consistent with spectroscopic evidence, the structure of **1**, consists of an $Ru_3$ triangle with two of the edges bridged by dppa ligands. The metal triangle and the two five-membered metallacycles are close to forming a plane. A least-squares calculation of the best planes formed by the nine atoms was carried out and the largest deviations from planarity are 0.01423 [P(1)] and 0.1315 Å [N(1)]. The coplanarity of the rings formed by dppa bridging a metal–metal edge had already been observed in $[CoPd_2(\mu_3\text{-}CO)_2(\mu_2\text{-}\{(Ph_2P)_2N(CH_3)\}_3]PF_6$ [4] and in $[Ru_3(\mu_3\text{-}E)_2\{\mu_2\text{-}P,P'\text{-}(PPh_2)_2NH\}(CO)_7]$ (E = S, Se) [8] but it is important to establish that the dppa-bridged edge is very long in the last compound and presumably does not hold a metal–metal bond, thus allowing larger flexibility of the metallacyclic ring formed. Non-planarity has also been observed in $[Ru_4(\mu_3\text{-}E)_2\{\mu_2\text{-}P,P'\text{-}(PR_2)_2NH\}(CO)_9]$.

Two of the metal–metal distances in **1** are identical while the third one, bridged by one of the dppa ligands, is only slightly longer (2.823(2) versus 2.833(3) Å) (see Table 1). These values are very similar to those described for the 'supported' metal–metal bonds in $[Ru_3(CO)_8(dppm)_2]$ [9]. All Ru–P bonds in **1** are equivalent and are also similar to those in the dppm analogue.

Bond parameters within the dppa ligand show some interesting trends. Both ligands have a P–N bond longer than the other one within the same dppa fragment (1.728(9) and 1.660(10) Å in one ligand and 1.724(9) and 1.674(10) Å in the other, values shorter and longer than the one observed in the free ligand (1.692(2) Å)), although the large standard deviations in the values in **1** do not allow a clear difference to be assured. Similar behavior was observed in $[Pd_4(\mu\text{-}Cl)_2(\mu\text{-}dppm)_2(\mu\text{-}dppa)_2](PF_6)_2$ [4] but no significant differences are observed in either $[Co_2Pt(\mu_3\text{-}CO)(CO)_6(\mu\text{-}dppa)]$ [10], $[Ru_3(CO)_{10}\{\mu\text{-}Ph_2PN(Et)PPh_2\}]$ [3], or $[Pt(dppa)_2][BF_4]_2 \cdot MeCN$ [2].

Five water molecules were found in the unit cell of **1** and an analysis of non-bonding distances shows the existence of a short contact (2.457 Å) between the hydrogen atom bonded to N(2) and the oxygen atom of one of the water molecules. This interaction might be a factor of influence in the almost planar conformation adopted by the metal–ligand cycles.

Crystals of **2** show crystallographically imposed symmetry and only half of the molecule is present in the asymmetric unit. As proposed, the structure consists of a triangle of ruthenium atoms with one of the edges bridged by a dppa ligand. The edge supported by the chelate ligand is slightly shorter than the other two (2.8287(11) versus 2.8545(10) Å), which are equivalent. This trend is similar to that observed in the structures of $[Ru_3(CO)_{10}(dppm)]$ [11] and of $[Ru_3(CO)_{10}\{\mu\text{-}Ph_2PN(Et)PPh_2\}]$ [3], although the difference between Ru–Ru distances is not as large as that observed in the second compound.

The chelate ring in this structure is twisted. The P(1)–Ru(1)–Ru(1a)–P(1a) torsion angle is 20.35°. Phosphorus–ruthenium distances are similar to those in **1** and in the $Ph_2PN(Et)PPh_2$ derivative, although they are longer than in $[Ru_3(CO)_{10}(dppm)]$. This could be explained in terms of lower backbonding towards the phosphorus atom. P–N distances are somewhat longer than those in the free ligand [12] and within the range of those observed in other dppa complexes [5,10].

## 3. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 136343 for compound **1** and 136342 for compound **2**. Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

## Acknowledgements

We thank CONACYT for grants (to G.S.C. and E.V.G.B.) and for support towards the acquisition of an X-ray diffractometer (Project F00084) and NMR spectrometers (Projects F563 and 166-0/PAD).

## References

[1] S. Browning, D.H. Farrar, J. Chem. Soc. Dalton Trans. (1995) 521.

[2] S. Browning, D.H. Farrar, M.R. Peterson, J. Mol. Struct. 251 (1991) 153.

[3] W. Engel, K.G. Moodley, L. Subramony, R.J. Haines, J. Organomet. Chem. 349 (1988) 393.

---

[2] X-ray data for both compounds were collected in a CAD4, Enraf–Nonius diffractometer in crystals mounted in capillary tubes. Both structures were solved by direct methods using SHELX-93 [14]. All non-hydrogen atoms were found in Fourier maps and refined anisotropically. Hydrogen atoms from phenyl groups were fixed in idealized positions and their positions refined. All calculations were carried out on computers. Compound **1**. $C_{56}H_{52}N_2O_{13}P_4Ru_3$, F.W. 1388.05, monoclinic, $P2_1/c$. $a = 16.629(3)$, 15.724(3), $c = 23.653(5)$ Å, $\beta = 94.22°$. $V = 6167.9$ Å$^3$. $\mu = 0.888$. $2\theta$ Range 2–49.96°. 10 624 unique reflections, 4475 observed ($>4\sigma$), $R = 0.0819$, $wR = 0.2152$. Compound **2** $C_{34}H_{21}N_1O_{10}P_2Ru_3 \cdot C_2H_2Cl_6$, F.W. = 1207.40, monoclinic, $C2/c$. $a = 21.657(4)$, $b = 15.142(3)$, $c = 17.087(3)$ Å, $\beta = 126.48(3)$, $V = 4505.4(15)$ Å$^3$. $Z = 4$, $\mu = 1.472$. $2\theta$ Range 2–49.94°, 3741 unique reflections, 2836 observed reflections ($>4\sigma$). $R = 0.0493$, $wR = 0.1408$.

[4] I. Bachert, P. Braunstein, M.K. McCart, F. Fabrizi de Biani, F. Laschi, P. Zanello, G. Kickelbick, U. Schubert, J. Organomet. Chem. 573 (1999) 47.
[5] I. Bachert, P. Braunstein, E. Guillon, C. Massera, J. Rosé, A. DeCian, J. Fischer, J. Cluster Sci. 10 (1999) 445.
[6] B. Ambwani, S. Chawla, A. Pöe, Inorg. Chem. 24 (1985) 2635.
[7] A. Cotton, B.E. Hanson, Inorg. Chem. 16 (1977) 3369.
[8] (a) E.V. García-Baez, M.J. Rosales-Hoz, H. Nöth, I. Haiduc, C. Silvestru, Inorg. Chem. Commun., submitted for publication. (b) A.M.Z. Slawin, M.B. Smith, D. Woollins, J. Chem. Soc. Dalton Trans. (1997) 1877.
[9] G. Lavigne, N. Lugan, J.-J. Bonnet, Acta Crystallogr. Sect. B 38 (1982) 1911.
[10] I. Bachert, I. Bartusseck, P. Braunstein, E. Guillon, J. Rosé, G. Kickelbick, J. Organomet. Chem. 580 (1999) 257.
[11] W. Coleman, D.F. Jones, P.H. Dixneuf, C. Brisson, J.-J. Bonnet, G. Lavigne, Inorg. Chem. 23 (1984) 952.
[12] H. Nöth, E. Fluck, Z. Naturforsch. Teil B 39 (1984) 744.
[13] M Bruce, T.W. Hambley, B.K. Nicholson, M.R. Snow, J. Organomet. Chem. 235 (1982) 83.
[14] (a) G.M. Sheldrick, SHELX-93, Program for Crystal Structure Refinement, Institut für Anorganische Chemie der Universität, Tammananstrasse 4, D-3400, Göttingen, Germany, 1993. (b) G.M. Sheldrick, SHELXS-86, Program for Crystal Structure Refinement, Institut für Anorganische Chemie der Universität, Tammananstrasse 4, D-3400, Göttingen, Germany, 1993.