

Crescent-Shaped Rhodium(I) Complexes with Bis(*o*-carboxymethylphenyl)triazenideCristina Tejel,<sup>\*†</sup> Miguel A. Ciriano,<sup>†</sup> Gustavo Ríos-Moreno,<sup>†</sup> Isabel T. Dobrinovitch,<sup>†</sup> Fernando J. Lahoz,<sup>†</sup> Luis A. Oro,<sup>†</sup> and Miguel Parra-Hake<sup>‡</sup>

Departamento de Química Inorgánica, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza-CSIC, E-50009 Zaragoza, Spain, and Centro de Graduados e Investigación, Instituto Tecnológico de Tijuana, Blvd. Industrial S/N. Mesa de Otay, 22510 Tijuana, Baja California, México

Received March 10, 2004

Reaction of  $[\{\text{Rh}(\mu\text{-Cl})(\text{CO})_2\}_2]$  with the triazene  $\text{ArNNNHAr}$  ( $\text{Ar} = o\text{-CO}_2\text{MeC}_6\text{H}_4$ ) produced the mononuclear complex  $[\text{RhCl}(\text{ArNNNHAr})(\text{CO})_2]$  (**1**). Complex **1** reacted with KOH in methanol to give the dinuclear compound  $[\{\text{Rh}(\mu\text{-ArNNNHAr})(\text{CO})_2\}_2]$  (**2**), which showed a “ $\mu\text{-}(1\kappa\text{N}^1, 2\kappa\text{N}^3)\text{-ArNNNHAr}$ ” coordination mode for both bridging ligands. The dinuclear complex  $[\{\text{Rh}(\mu\text{-ArNNNHAr})(\text{CO})_2\}_2]$  (**2**) easily undergoes redistribution reactions in which the eight-membered “ $\text{Rh}_2(\text{NNN})_2$ ” core is broken. Thus, reaction of **2** with the anionic complex  $(\text{NHEt}_3)[\text{RhCl}_2(\text{CO})_2]$  gave the single-bridged complex  $(\text{NHEt}_3)[\text{Rh}_2(\mu\text{-ArNNNHAr})\text{Cl}_2(\text{CO})_4]$  (**4**), while the trinuclear complexes  $[\text{Rh}_3(\mu\text{-ArNNNHAr})(\mu\text{-Cl})(\mu\text{-CO})\text{Cl}(\text{CO})_4]$  (**5**) and  $[\text{Rh}_3(\mu\text{-ArNNNHAr})_2(\mu\text{-Cl})(\mu\text{-CO})(\text{CO})_3]$  (**6**) were isolated by addition of the neutral compound  $[\{\text{Rh}(\mu\text{-Cl})(\text{CO})_2\}_2]$  to **2**, depending on the molar ratio employed. The formation of **5** and **6** involved the loss of carbonyl groups and the coordination of the oxygen atoms of the  $\text{CO}_2\text{Me}$  groups. The structures of **4**, **5**, and **6** have been determined by X-ray diffraction methods, which show the ability of bis(*o*-carboxymethylphenyl)-triazenide to act as bi-, tri-, and tetra-dentate ligand-spanning dinuclear moieties in trinuclear complexes.

## Introduction

The bis(aryl)triazenide anions  $(\text{ArNNNHAr})^-$  are “short-bite” ligands understudied when compared with their related diphosphines, 2-pyridylphosphines,<sup>1</sup> and anionic N–C–X ( $\text{X} = \text{N}, \text{O}, \text{S}$ ) type ligands,<sup>2</sup> although a number of studies on complexes of these ligands with rhodium and iridium in different oxidation states have been reported. Derivatives of Rh and Ir in the oxidation state III are the homoleptic mononuclear compounds  $[\text{M}(\text{ArNNNHAr})_3]$ , with the three ligands acting in an  $\text{N}, \text{N}'$ -chelating mode,<sup>3</sup> while the reported complexes of Rh in the oxidation state II are dinuclear with a “lantern-type” structure with four triazenide bridges, as found in  $[\text{Rh}_2(\mu\text{-ArNNNHAr})_4]$ .<sup>4</sup> However, most of the

chemistry of Rh and Ir with these ligands concerns the oxidation state I. Although mononuclear complexes of these  $d^8$  ions with terminal<sup>5</sup> and chelating<sup>6</sup> triazenide ligands are known, the triazenide anions typically adopt the bridging mode observed in homodinuclear<sup>7–9</sup> and heterodinuclear Rh/Ir,<sup>10</sup> Rh/Hg and Ir/Hg<sup>11</sup> “face-to-face” compounds. The high stability of the eight-membered “ $\text{M}_2(\mu\text{-ArNNNHAr})_2$ ” core in the homodinuclear complexes has allowed the development of a rich redox-chemistry involving a combination of theoretical studies with electrochemistry and ESR spectroscopy.<sup>12</sup> For example, the “face-to-face” dirhodium structure remained intact after one electron oxidation reaction<sup>13,14</sup> to the corresponding paramagnetic monocations (formally  $\text{M}(\text{I})/$

\* To whom correspondence should be addressed. E-mail: ctejel@posta.unizar.es. Fax: (+34) 976-761187.

<sup>†</sup> Departamento de Química Inorgánica, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza-CSIC.

<sup>‡</sup> Centro de Graduados e Investigación, Instituto Tecnológico de Tijuana.

(1) Zhang, Z.-Z.; Cheng, H. *Coord. Chem. Rev.* **1996**, *147*, 1.  
(2) Oro, L. A.; Ciriano, M. A.; Pérez-Torrente, J. J.; Villarroya, B. E. *Coord. Chem. Rev.* **1999**, *195*, 941.  
(3) Colson, S. F.; Robinson, S. D. *Polyhedron* **1990**, *9*, 1737.  
(4) Hursthouse, M. B.; Mazid, M. A.; Clark, T.; Robinson, D. *Polyhedron* **1993**, *12*, 563.

(5) Immirzi, A.; Porzio, W.; Bombieri, G.; Toniolo, L. *J. Chem. Soc., Dalton Trans.* **1980**, 1098.

(6) Carriedo, C.; Connelly, N. G.; Hettrich, R.; Orpen, A. G.; White, J. M. *J. Chem. Soc., Dalton Trans.* **1989**, 745.

(7) Knoth, W. H. *Inorg. Chem.* **1973**, *12*, 38.

(8) Connelly, N. G.; Daykin, H.; Demidowicz, Z. *J. Chem. Soc., Dalton Trans.* **1978**, 1532.

(9) Connelly, N. G.; García, G. *J. Chem. Soc., Dalton Trans.* **1987**, 2737.

(10) Connelly, N. G.; Hayward, O. D.; Klanginsirikul, P.; Orpen, A. G.; Rieger, P. H. *Chem. Commun.* **2000**, 963.

(11) Van Vliet, P. I.; Kokkes, M.; Van Koten, G.; Vrieze, K. *J. Organomet. Chem.* **1980**, *187*, 413.

M(II) complexes), and a recent study<sup>15</sup> on dinuclear complexes with a family of triazenide ligands of the type (*p*-XC<sub>6</sub>H<sub>4</sub>)NNN(*p*-X'C<sub>6</sub>H<sub>4</sub>) showed the marked influence of the X and X' groups on the oxidation potential E<sup>o</sup>. Moreover, the geometrically asymmetric triazenido-bridged complex [(CO)<sub>2</sub>Rh(*μ*-ArNNNAr)<sub>2</sub>Rh(bipy)]<sup>16</sup> was found to be a precursor to a wide range of redox-active species,<sup>17</sup> allowing the observation of processes such as the redox-isomerization of a triazenide bridge “*μ*-(1κN<sup>1</sup>,2κN<sup>3</sup>)-ArNNNAr” into “*μ*-(1κN<sup>1</sup>,1:2κN<sup>3</sup>)-ArNNNAr”<sup>18</sup> and the equilibrium between the cores “Rh(II)(*μ*-ArNNNAr)<sub>2</sub>Rh(II)(CO)” and “Rh(III)-(*μ*-ArNNNAr)<sub>2</sub>(*μ*-CO)Rh(III)”.<sup>19,20</sup> In addition, the triply bridged paramagnetic Rh(I)/Rh(II) complex [Rh<sub>2</sub>(*μ*-ArNNNAr)<sub>3</sub>(CO)<sub>2</sub>] has been recently reported.<sup>21</sup> A noteworthy point is that the bis(aryl)triazenide ligands involved on the Rh and Ir chemistry overviewed here are the simplest PhNNNPh<sup>-</sup> anion and its *para*-substituted derivatives.

The incorporation of different groups (X) at the *ortho* position of the aryl ring of the bis(aryl)triazenide ligand with donor properties could produce a markedly different coordination chemistry. For example, these functionalized aryltriazenides could span a dinuclear unit to form cavity shaped ligands, as reported for 2,7-bis(2'-pyridyl)-1,8-naphthyridine.<sup>22,23</sup> Moreover, a hemilabile behavior could be observed if the X groups were poorly coordinating donors toward soft metal centers, such as the oxygen from an ester group. Therefore, it seemed to us that the scarcely studied bis(*o*-carboxymethylphenyl)triazene<sup>24</sup> would be a useful ligand to test the above-mentioned properties with rhodium complexes, and we report here our results on this topic.

## Experimental Section

**Starting Materials and Physical Methods.** All reactions were carried out under argon using standard Schlenk techniques. The compounds [{Rh(*μ*-Cl)(CO)<sub>2</sub>]<sub>2</sub><sup>25</sup> and bis(*o*-carboxymethylphenyl)triazene<sup>26</sup> were prepared according to literature methods. Solvents

were dried and distilled under argon before use by standard methods. Carbon, hydrogen, and nitrogen analyses were performed with a Perkin-Elmer 2400 microanalyzer. IR spectra were recorded with a Nicolet 550 spectrophotometer. Mass spectra were recorded in a VG Autospec double-focusing mass spectrometer operating in the FAB<sup>+</sup> mode. Ions were produced with the standard Cs<sup>+</sup> gun at ca. 30 kV, 3-nitrobenzyl alcohol (NBA) was used as matrix. <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra were recorded on a Bruker ARX 300 and on a Varian UNITY 300 spectrometers operating at 300.13 and 299.95 MHz for <sup>1</sup>H, respectively. Chemical shifts are reported in parts per million and referenced to SiMe<sub>4</sub> using the residual signal of the deuterated solvent as reference. Conductivities were measured in acetone solutions using a Philips PW 9501/01 conductimeter.

### Synthesis of the Complexes. [RhCl(ArNNNAr)(CO)<sub>2</sub>] (1).

A saturated solution of ArNNNAr (163.0 mg, 0.52 mmol) in diethyl ether (3 mL) was added dropwise to a solution of [{Rh(*μ*-Cl)(CO)<sub>2</sub>]<sub>2</sub> (101.0 mg, 0.26 mmol) in hexane (15 mL). A yellow microcrystalline solid precipitated almost immediately. The suspension was concentrated to ca. 5 mL and the solution was decanted. The solid was washed with hexane (5 mL) and vacuum-dried. Yield: 216 mg (82%). Anal. Calcd for C<sub>18</sub>H<sub>15</sub>N<sub>3</sub>ClO<sub>6</sub>Rh: C, 42.58; H, 2.98; N, 8.28. Found: C, 42.65; H, 3.14; N, 8.39. IR (KBr, cm<sup>-1</sup>): ν(CO) 2089 (s), 2025 (s); ν(C=O) 1721 (s), 1702 (m). <sup>1</sup>H NMR (-73 °C, CD<sub>2</sub>Cl<sub>2</sub>) δ: 14.36 (s, 1H, NH); 8.09 (d, *J*<sub>HH</sub> = 7.9 Hz, 1H), 8.07 (d, *J*<sub>HH</sub> = 7.9 Hz, 1H), 7.76 (d, *J*<sub>HH</sub> = 7.5 Hz, 1H), 7.63 (t, *J*<sub>HH</sub> = 7.7 Hz, 1H), 7.56 (m, 2H), 7.49 (t, *J*<sub>HH</sub> = 7.7 Hz, 1H) and 7.26 (td, *J*<sub>HH</sub> = 8.1, 2.1 Hz, 1H) (C<sub>6</sub>H<sub>4</sub>); 4.00 (s, 3H) and 3.63 (s, 3H) (CO<sub>2</sub>Me). <sup>13</sup>C{<sup>1</sup>H} NMR (-73 °C, CD<sub>2</sub>Cl<sub>2</sub>) δ: 183.9 (d, *J*<sub>CRh</sub> = 67 Hz) and 179.2 (d, *J*<sub>CRh</sub> = 73 Hz) (Rh-CO); 168.3 and 168.2 (CO<sub>2</sub>Me); 147.6, 141.0, 135.9, 132.8, 131.9, 131.2, 129.4, 126.8, 126.0, 125.6, 115.4 and 114.8 (C<sub>6</sub>H<sub>4</sub>); 54.0 and 53.5 (CO<sub>2</sub>Me). MS (FAB<sup>+</sup>, CH<sub>2</sub>Cl<sub>2</sub>, *m/z*): 472, 100% (M<sup>+</sup> - Cl), 444, 45% (M<sup>+</sup> - Cl - CO).

**[{Rh(*μ*-ArNNNAr)(CO)<sub>2</sub>]<sub>2</sub> (2).** To a solution of [RhCl(ArNNNAr)(CO)<sub>2</sub>] (1) (264.0 mg, 0.52 mmol) in diethyl ether (10 mL) was added dropwise a solution of KOH in methanol (0.52 mmol in 2.0 mL). The initial yellow solution turned purple immediately. The solution was stirred for 10 min and evaporated to dryness. The residue was extracted with several portions of hexane (10 mL), filtered over Celite, and evaporated to dryness. The purple microcrystalline material was vacuum-dried. Yield: 218 mg (89%). Anal. Calcd for C<sub>36</sub>H<sub>28</sub>N<sub>6</sub>O<sub>12</sub>Rh<sub>2</sub>: C, 45.88; H, 2.99; N, 8.92. Found: C, 45.76; H, 3.11; N, 8.93. IR (hexane, cm<sup>-1</sup>): ν(CO) 2094 (s), 2067 (m), 2031 (s); ν(C=O) 1735 (s). <sup>1</sup>H NMR (25 °C, C<sub>6</sub>D<sub>6</sub>) δ: 7.80 (d, *J*<sub>HH</sub> = 8.1 Hz, 4H), 7.50 (d, *J*<sub>HH</sub> = 7.7 Hz, 4H), 7.00 (t, *J*<sub>HH</sub> = 7.7 Hz, 4H) and 6.76 (t, *J*<sub>HH</sub> = 7.5 Hz, 4H) (C<sub>6</sub>H<sub>4</sub>); 3.29 (s, 12H) (CO<sub>2</sub>Me). <sup>13</sup>C{<sup>1</sup>H} NMR (25 °C, C<sub>6</sub>D<sub>6</sub>) δ: 184.7 (d, *J*<sub>CRh</sub> = 67 Hz) (Rh-CO); 167.8 (CO<sub>2</sub>Me); 150.5, 130.9, 130.3, 127.2, 127.0 and 125.6 (C<sub>6</sub>H<sub>4</sub>); 51.6 (CO<sub>2</sub>Me). MS (FAB<sup>+</sup>, CH<sub>2</sub>Cl<sub>2</sub>, *m/z*): 886, 10% (M<sup>+</sup> - 2CO), 858, 100% (M<sup>+</sup> - 3CO).

**(NH<sub>4</sub>)<sub>3</sub>[RhCl<sub>2</sub>(CO)<sub>2</sub>] (3).** Solid NH<sub>4</sub>Cl (71.5 mg, 0.52 mmol) was added to a solution of [{Rh(*μ*-Cl)(CO)<sub>2</sub>]<sub>2</sub> (101.0 mg, 0.26 mmol) in diethyl ether (5 mL) to give a pale yellow solution in 10 min. The solution was evaporated to dryness, and the yellow residue was washed with hexane (2 × 5 mL) and vacuum-dried. Yield: 155 mg (90%). Anal. Calcd for C<sub>8</sub>H<sub>16</sub>NCl<sub>2</sub>O<sub>2</sub>Rh: C, 28.94; H, 4.86; N, 4.22. Found: C, 29.12; H, 5.12; N, 4.37. IR (diethyl ether, cm<sup>-1</sup>): ν(CO) 2073 (s), 1999 (s). <sup>1</sup>H NMR (-73 °C, CD<sub>2</sub>Cl<sub>2</sub>) δ: 7.82 (br s, 1H, NH); 3.12 (m, 6H, CH<sub>2</sub>); 1.25 (t, *J*<sub>HH</sub> = 7.2 Hz, 9H, CH<sub>3</sub>).

- (12) Boyd, D. C.; Connelly, N. G.; García Herbosa, G.; Hill, M. G.; Mann, K. R.; Mealli, C.; Orpen, A. G.; Richardson, K. E.; Rieger, P. H. *Inorg. Chem.* **1994**, *33*, 960.
- (13) Connelly, N. G.; Finn, C. J.; Freeman, M. J.; Orpen, A. G.; Stirling, J. J. *Chem. Soc., Chem. Commun.* **1984**, 1025.
- (14) Connelly, N. G.; García, G.; Gilbert, M.; Stirling, J. S. *J. Chem. Soc., Dalton Trans.* **1987**, 1403.
- (15) Connelly, N. G.; Davis, P. R. G.; Harry, E. E.; Klanginsirikul, P.; Venter, M. J. *Chem. Soc., Dalton Trans.* **2000**, 2273.
- (16) Connelly, N. G.; García, G. *J. Chem. Soc., Chem. Commun.* **1987**, 246.
- (17) Brauns, T.; Carriedo, C.; Goekayne, J. S.; Connelly, N. G.; García-Herbosa, G.; Orpen, A. G. *J. Chem. Soc., Dalton Trans.* **1989**, 2049.
- (18) Connelly, N. G.; Hopkins, P. M.; Orpen, A. G.; Rosair, G. M.; Viguri, F. J. *Chem. Soc., Dalton Trans.* **1992**, 2907.
- (19) Connelly, N. G.; Einig, T.; García Herbosa, G.; Hopkins, P. M.; Mealli, C.; Orpen, A. G.; Rosair, G. M. *J. Chem. Soc., Chem. Commun.* **1992**, 143.
- (20) Connelly, N. G.; Einig, T.; García Herbosa, G.; Hopkins, P. M.; Mealli, C.; Orpen, A. G.; Rosair, G. M.; Viguri, F. J. *Chem. Soc., Dalton Trans.* **1994**, 2025.
- (21) Connelly, N. G.; Hayward, O. D.; Klanginsirikul, P.; Orpen, A. G. *J. Chem. Soc., Dalton Trans.* **2002**, 305.
- (22) Campos-Fernández, C. S.; Thomson, L. M.; Galán-Mascarós, J. R.; Ouyang, X.; Dunbar, K. R. *Inorg. Chem.* **2002**, *41*, 1523.
- (23) Tikkanen, W. R.; Binamira-Soriaga, E.; Kaska, W. C.; Ford, P. C. *Inorg. Chem.* **1983**, *22*, 1147.
- (24) Ríos-Moreno, G.; Aguirre, G.; Parra-Hake, M.; Walsh, P. J. *Polyhedron* **2003**, *22*, 563.
- (25) McCleverty, J. A.; Wilkinson, G. *Inorg. Synth.* **1966**, *8*, 211.

- (26) Vermin, G.; Siv, C.; Metzger, Y. J. *Synthesis* **1977**, *10*, 691.

**Table 1.** Crystal Data and Refinement Parameters for Complexes **4**, **5**, and **6**

	<b>4</b>	<b>5</b>	<b>6</b>
empirical formula	C <sub>26</sub> H <sub>30</sub> Cl <sub>2</sub> N <sub>4</sub> O <sub>8</sub> Rh <sub>2</sub>	C <sub>21</sub> H <sub>14</sub> Cl <sub>2</sub> N <sub>3</sub> O <sub>9</sub> Rh <sub>3</sub>	C <sub>36</sub> H <sub>28</sub> ClN <sub>6</sub> O <sub>12</sub> Rh <sub>3</sub>
fw	803.26	831.98	1080.82
space group	<i>P</i> 2 <sub>1</sub> / <i>c</i> (No. 14)	<i>P</i> $\bar{1}$ (No. 2)	<i>P</i> $\bar{1}$ (No. 2)
<i>a</i> , Å	19.5308(13)	9.5760(6)	9.0715(7)
<i>b</i> , Å	9.9136(7)	9.7734(6)	11.2733(9)
<i>c</i> , Å	33.023(2)	14.6622(9)	20.0489(16)
$\alpha$ , deg	90.0	94.9420(10)	84.2820(10)
$\beta$ , deg	98.3400(10)	92.9820(10)	83.1200(10)
$\gamma$ , deg	90.0	108.7770(10)	68.8380(10)
<i>V</i> , Å <sup>3</sup> / <i>Z</i>	6326.3(7)/8	1289.74(14)/2	1894.8(3)/2
<i>D</i> <sub>calcd</sub> , g·cm <sup>-3</sup>	1.687	2.142	1.894
$\mu$ , mm <sup>-1</sup>	1.264	2.160	1.434
no data/restraints/params	11172/0/769	5997/0/357	8662/0/550
GOF (all data) <sup>a</sup>	1.033	0.973	1.024
<i>R</i> <sub>1</sub> ( <i>F</i> )	0.0492 (7556 reflns)	0.0303 (4941 reflns)	0.0463 (6752 reflns)
(only for <i>F</i> <sup>2</sup> > 2 $\sigma$ ( <i>F</i> <sup>2</sup> )) <sup>b</sup>			
<i>wR</i> <sub>2</sub> ( <i>F</i> <sup>2</sup> ) (all data) <sup>c</sup>	0.1102	0.0561	0.1019

<sup>a</sup> GOF =  $(\sum[w(F_o^2 - F_c^2)^2]/(n - p))^{1/2}$ , where *n* and *p* are the number of data and parameters. <sup>b</sup> *R*<sub>1</sub>(*F*) =  $\sum||F_o| - |F_c||/\sum|F_o|$  only for observed reflections (in parentheses). <sup>c</sup> *wR*<sub>2</sub>(*F*<sup>2</sup>) =  $(\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2])^{1/2}$  where  $w = 1/[\sigma^2(F_o^2) + (aP)^2]$  and  $P = [\max(0, F_o^2) + 2F_c^2]/3$ .

<sup>13</sup>C{<sup>1</sup>H} NMR (−73 °C, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$ : 181.3 (d, *J*C*Rh* = 73 Hz, Rh–CO); 46.2 (CH<sub>2</sub>); 9.97 (CH<sub>3</sub>).

(NHEt<sub>3</sub>)[Rh<sub>2</sub>( $\mu$ -ArNNAr)Cl<sub>2</sub>(CO)<sub>4</sub>] (**4**). The addition of neat triethylamine (36.2  $\mu$ L, 0.26 mmol) to a mixture of [Rh( $\mu$ -Cl)(CO)<sub>2</sub>]<sub>2</sub> (101.0 mg, 0.26 mmol) and ArNNHAr (81.5 mg, 0.26 mmol) in diethyl ether (6 mL) caused the immediate formation of a purple solution, from which an orange solid crystallized in 10 min. This mixture was evaporated to dryness and then the residue was stirred with hexane (5 mL) to give an orange solid and a pale-orange solution. The solution was decanted and the solid was washed with hexane (6 mL) and vacuum-dried. Yield: 205 mg (98%). Single crystals of **4** were obtained by layering a purple solution of the compound in diethyl ether with hexane. Anal. Calcd for C<sub>26</sub>H<sub>30</sub>N<sub>4</sub>Cl<sub>2</sub>O<sub>8</sub>Rh<sub>2</sub>: C, 38.87; H, 3.76; N, 6.97. Found: C, 38.89; H, 3.35; N, 7.20. IR (KBr, cm<sup>-1</sup>):  $\nu$ (CO) 2074 (s), 2058 (s), 1996 (s);  $\nu$ (C=O) 1732 (m), 1707 (m).

[Rh<sub>3</sub>( $\mu$ -ArNNAr)( $\mu$ -Cl)( $\mu$ -CO)Cl(CO)<sub>4</sub>] (**5**). A solution of [Rh( $\mu$ -ArNNAr)(CO)<sub>2</sub>]<sub>2</sub> (**2**) (47.1 mg, 0.05 mmol) in hexane (10 mL) was added dropwise to a solution of [Rh( $\mu$ -Cl)(CO)<sub>2</sub>]<sub>2</sub> (38.9 mg, 0.10 mmol) in the same solvent (5 mL). The resulting dark-red solution was maintained undisturbed for 12 h to render the title compound as red-violet crystals. The solution was decanted and the crystals were washed with hexane and vacuum-dried. Yield: 71 mg (85%). Anal. Calcd for C<sub>21</sub>H<sub>14</sub>N<sub>3</sub>Cl<sub>2</sub>O<sub>9</sub>Rh<sub>3</sub>: C, 30.32; H, 1.70; N, 5.05. Found: C, 30.18; H, 1.56; N, 4.95. IR (KBr, cm<sup>-1</sup>):  $\nu$ (CO) 2072 (s), 2038 (m), 2003 (s);  $\nu$ ( $\mu$ -CO) 1849 (m), 1839 (m);  $\nu$ (C=O) 1651 (m), 1624 (m). <sup>1</sup>H NMR (25 °C, CDCl<sub>3</sub>)  $\delta$ : 8.04 (d, *J*HH = 8.1 Hz, 2H), 7.53 (td, *J*HH = 6.6, 1.5 Hz, 2H), 7.37 (d, *J*HH = 8.4 Hz, 2H) and 7.29 (t, *J*HH = 7.2 Hz, 2H) (C<sub>6</sub>H<sub>4</sub>); 4.13 (s, 6H, CO<sub>2</sub>Me). MS (FAB<sup>+</sup>, CH<sub>2</sub>Cl<sub>2</sub>, *m/z*): 602, 70% ([Rh<sub>2</sub>( $\mu$ -ArNNAr)( $\mu$ -CO)(CO)<sub>2</sub>]<sup>+</sup>), 577, 90% ([Rh<sub>2</sub>( $\mu$ -ArNNAr)( $\mu$ -CO)(CO)<sub>2</sub>]<sup>+</sup>).  $\Lambda_M$  (3.45  $\times 10^{-4}$  M in acetone) = 20 S cm<sup>2</sup> mol<sup>-1</sup>.

[Rh<sub>3</sub>( $\mu$ -ArNNAr)<sub>2</sub>( $\mu$ -Cl)( $\mu$ -CO)(CO)<sub>3</sub>] (**6**). A solution of [Rh( $\mu$ -Cl)(CO)<sub>2</sub>]<sub>2</sub> (11.6 mg, 0.03 mmol) in hexane (5 mL) was dropwise added to a solution of [Rh( $\mu$ -ArNNAr)(CO)<sub>2</sub>]<sub>2</sub> (**2**) (56.5 mg, 0.06 mmol) in the same solvent (10 mL). After 3 h, a brown solid started to crystallize and the suspension was left at −30 °C overnight. The solution was decanted and the crystals were washed with hexane and vacuum-dried. Yield: 58 mg (89%). Anal. Calcd for C<sub>36</sub>H<sub>28</sub>N<sub>6</sub>ClO<sub>12</sub>Rh<sub>3</sub>: C, 40.01; H, 2.61; N, 7.78. Found: C, 39.96; H, 2.49; N, 7.53. IR (CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>):  $\nu$ (CO) 2070 (s), 2011 (s), 1992 (s);  $\nu$ ( $\mu$ -CO) 1826 (s);  $\nu$ (C=O) 1723 (m), 1712 (m), 1652 (m), 1630 (s). <sup>1</sup>H NMR (25 °C, CDCl<sub>3</sub>)  $\delta$ : 8.00 (d, *J*HH =

7.4 Hz, 1H), 7.88 (t, *J*HH = 7.4 Hz, 1H), 7.82 (d, *J*HH = 7.8 Hz, 1H), 7.75 (d, *J*HH = 7.0 Hz, 1H), 7.65 (d, *J*HH = 7.2 Hz, 1H), 7.74–7.22 (m, 8H), 7.18 (t, *J*HH = 7.5 Hz, 1H), 7.10 (d, *J*HH = 7.9 Hz, 1H), 7.02 (d, *J*HH = 7.5 Hz, 1H) (C<sub>6</sub>H<sub>4</sub>); 4.03 (s, 3H), 3.95 (s, 3H), 3.70 (s, 3H) and 3.54 (s, 3H) (CO<sub>2</sub>Me). MS (FAB<sup>+</sup>, CH<sub>2</sub>Cl<sub>2</sub>, *m/z*): 1017, 26% (M<sup>+</sup> – Cl – CO), 989, 55% (M<sup>+</sup> – Cl – 2CO), 961, 100% (M<sup>+</sup> – Cl – 3CO).

**Structural Determination of compounds 4, 5, and 6.** A summary of crystal data and refinement parameters for the structural analyses is given in Table 1. The crystals used in the analyses (orange block 0.20  $\times$  0.11  $\times$  0.07 mm (**4**), red block 0.17  $\times$  0.17  $\times$  0.12 (**5**), and a red lamina 0.16  $\times$  0.13  $\times$  0.06 mm (**6**)) were glued to a glass fiber and mounted on Bruker SMART APEX diffractometer. The instrument was equipped with CCD area detector and data were collected using graphite-monochromated Mo K $\alpha$  radiation ( $\lambda$  = 0.71073 Å) at low temperature (100 K). Cell constants were obtained from the least-squares refinement of three-dimensional centroids (6643 reflns, 2.3°  $\leq$   $\theta$   $\leq$  28.2° for **4**; 4971 reflns, 2.3°  $\leq$   $\theta$   $\leq$  28.0° for **5** and 4531 reflns, 2.3°  $\leq$   $\theta$   $\leq$  27.9° for **6**). Data were measured (61739 reflns, 1.1°  $\leq$   $\theta$   $\leq$  25.0° (**4**); 15845 reflns, 1.4°  $\leq$   $\theta$   $\leq$  28.6° (**5**); 22599 reflns, 1.9°  $\leq$   $\theta$   $\leq$  28.4° (**6**)) through the use of CCD recording of narrow  $\omega$  rotation frames (0.3° each), completing almost all reciprocal space in the stated  $\theta$  range. All data were integrated with the Bruker SAINT program, which includes Lorentz and polarization corrections. Absorption correction was applied by using the SADABS routine (min. max. transmission factors 0.731 and 0.914 (**4**), 0.708 and 0.789 (**5**), and 0.889 and 0.915 (**6**)).<sup>27</sup>

The structures were solved by Patterson methods, completed by subsequent difference Fourier techniques and refined by full-matrix least-squares on *F*<sup>2</sup> (SHELXL-97)<sup>28</sup> with initial isotropic, but subsequent anisotropic, thermal parameters for all non-hydrogen atoms. Hydrogen atoms were included in the model from observed (**5** and **6**) or calculated (**4**) positions, but were refined in all cases with riding positional and free displacement parameters. Atomic scattering factors were used as implemented in the program.<sup>28</sup>

(27) SAINTPLUS program, v. 6.28; Bruker AXS: Madison, WI 2001. Blessing, R. H. *Acta Crystallogr., Sect. A* **1995**, *51*, 33; implemented in SADABS: Area-detector absorption correction, v. 2.03; Bruker-AXS: Madison, WI, 2002.

(28) SHELXTL Package, v. 6.10; Bruker-AXS: Madison, WI, 2000. Sheldrick, G. M. SHELXS-86 and SHELXL-97; University of Göttingen: Göttingen, Germany, 1997.

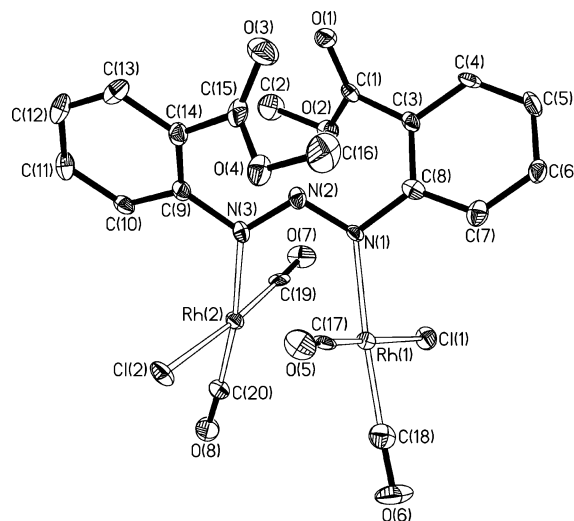
## Results and Discussion

Reaction of  $[\{\text{Rh}(\mu\text{-Cl})(\text{CO})_2\}_2]$  with the triazene ligand (*o*-CO<sub>2</sub>MeC<sub>6</sub>H<sub>4</sub>)NNNH(*o*-CO<sub>2</sub>MeC<sub>6</sub>H<sub>4</sub>), ArNNNHAr in the following discussion, produced the mononuclear compound  $[\text{RhCl}(\text{ArNNNHAr})(\text{CO})_2]$  (**1**), isolated as a yellow microcrystalline material. Analytical and spectroscopic data of **1** agreed with the proposed formulation. Thus, two strong  $\nu(\text{CO})$  bands in the IR spectrum (at 2089 and 2025 cm<sup>-1</sup>) indicated a *cis*-dicarbonyl moiety in **1**, while the CO<sub>2</sub>Me groups remained uncoordinated since there is no shift of the  $\nu(\text{C}=\text{O})$  bands relative to the free ligand. In addition, the <sup>1</sup>H NMR spectrum showed, along with the NH resonance (at 14.36 ppm), two inequivalent *o*-CO<sub>2</sub>MeC<sub>6</sub>H<sub>4</sub> groups, also detected in the <sup>13</sup>C{<sup>1</sup>H} NMR spectrum, that agreed with the monocoordination of the triazene ligand through the N<sup>3</sup> atom to the rhodium center.

Addition of one molar-equiv of KOH in methanol to a solution of **1** in diethyl ether caused the deprotonation of the triazene ligand with formation of the dinuclear complex  $[\{\text{Rh}(\mu\text{-ArNNNHAr})(\text{CO})_2\}_2]$  (**2**), which was isolated as a purple-red microcrystalline material. The mutually *cis* disposition of the two triazenide ligands in the face-to-face complex **2** was established from the observation of equivalent carbonyl and aryl groups in the <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra and the typical pattern of three  $\nu(\text{CO})$  bands for a dinuclear tetracarbonyl complex under C<sub>2v</sub> symmetry in the IR spectrum.

While the mononuclear complex  $[\text{RhCl}(\text{ArNNNHAr})(\text{CO})_2]$  reacted with KOH in methanol to cleanly give the dinuclear compound  $[\{\text{Rh}(\mu\text{-ArNNNHAr})(\text{CO})_2\}_2]$  (**2**), the result from the apparently similar reaction of **1** with NEt<sub>3</sub> was found to be quite different. Thus, addition of one molar-equiv of NEt<sub>3</sub> to a diethyl ether solution of **1** gave a purple solution whose IR spectrum showed the partial formation of **2** along with a new species (**3**) having two strong  $\nu(\text{CO})$  absorptions at 2073 and 1999 cm<sup>-1</sup>. From these solutions, an orange microcrystalline material (**4**) separated after stirring for 10 min. The IR spectrum of **4** in KBr pellets again showed three  $\nu(\text{CO})$  absorptions, but shifted ca. 20 cm<sup>-1</sup> to low frequencies relative to those of **2** and uncoordinated CO<sub>2</sub>Me groups, while solutions of **4** in toluene are purple and contain complexes **2** and **3**. Since **4** evolved in solution to **2** and **3**, the elucidation of the structure of **4** in the solid state was achieved from a X-ray diffraction study.

Compound **4** was found to contain the anionic dinuclear complex  $[\text{Rh}_2(\mu\text{-ArNNNHAr})\text{Cl}_2(\text{CO})_4]^-$ . Two crystallographically independent, formally enantiomeric, dinuclear complexes were detected in the crystal structure. Figure 1 shows the molecular structure of one of these anionic complexes together with the atomic numbering scheme; the most relevant bond distances and angles are collected in Table 2. In this dinuclear complex, one bis(*o*-carboxymethylphenyl)-triazenide group bridges the two rhodium atoms through the triazenide moiety, acting as a 3-electron donor ligand. Both rhodium atoms complete square-planar coordination spheres with two *cis* CO groups and a chloride ligand, the Rh–N (2.099(3) Å), Rh–C (1.850(3) Å), and Rh–Cl (2.3481(8)



**Figure 1.** Molecular structure of the dinuclear anionic complex  $[\text{Rh}_2(\mu\text{-ArNNNHAr})\text{Cl}_2(\text{CO})_4]^-$  (from **4**) (only one independent molecule is represented).

Å) are in the normal range. The relative conformation of the two square-planar rhodium atoms is slightly staggered, 26.6° approximately. The intramolecular rhodium–rhodium nonbonding distances, 2.9718(7) and 2.9628(7) Å, were observed to be similar to those found in related binuclear rhodium and iridium (I) neutral complexes bridged by two triazenide ligands (2.960(4) Å in  $[\text{Rh}_2(\mu\text{-RNNNR})_2(\text{CO})_2(\text{PPh}_3)_2]$  (R = *p*-tolyl),<sup>13</sup> or 2.8462(8) Å in  $[\text{Rh}(\text{cod})(\mu\text{-RNNNR})_2\text{Ir}(\text{CO})_2]$ <sup>10</sup>).

The structure shown in complex **4** is noteworthy since no previous reports on dinuclear anionic complexes of formula  $[\text{Rh}_2(\mu\text{-L})\text{Cl}_2(\text{CO})_4]^-$  (L = anionic ligand) have been described.<sup>29</sup> The closer dinuclear compounds were the neutral complexes derived from bridging hydrazine ligands  $[\text{Rh}_2(\mu\text{-L})\text{Cl}_2(\text{CO})_4]$  (L = RHNNHMe, R = H, Me) showing a slightly longer Rh–Rh distance of 3.208 Å.<sup>30</sup>

Since **4** contains one single bridging ligand in the solid state and transforms into the dinuclear compound  $[\{\text{Rh}(\mu\text{-ArNNNHAr})(\text{CO})_2\}_2]$  (**2**) together with compound **3** in solution, the *cis*-dicarbonyl species **3** should be the Vallarino's-type compound  $(\text{NHET}_3)[\text{RhCl}_2(\text{CO})_2]$  (**3**). To ensure this point, complex **3** was independently prepared by addition of two molar-equiv of NHET<sub>3</sub>Cl to a diethyl ether solution of  $[\{\text{Rh}(\mu\text{-Cl})(\text{CO})_2\}_2]$ . Analytical and spectroscopic data of **3** agreed with the proposed formulation (see Experimental Section). One relevant property of **3** is its high solubility in nonpolar solvents that could be explained assuming a zwitterionic character due to the formation of hydrogen bonds between the HN proton from the cation and the chloride ligands from the anion. In fact, the NHET<sub>3</sub><sup>+</sup> cation was found to be able to form such bonds in related anionic mononuclear rhodium complexes.<sup>31</sup>

Once complexes **2**, **3**, and **4** were identified, the formation of **4** by addition of NEt<sub>3</sub> to **1** could be explained according

(29) Allen, F. H. *Acta Crystallogr.* **2002**, B58, 380.

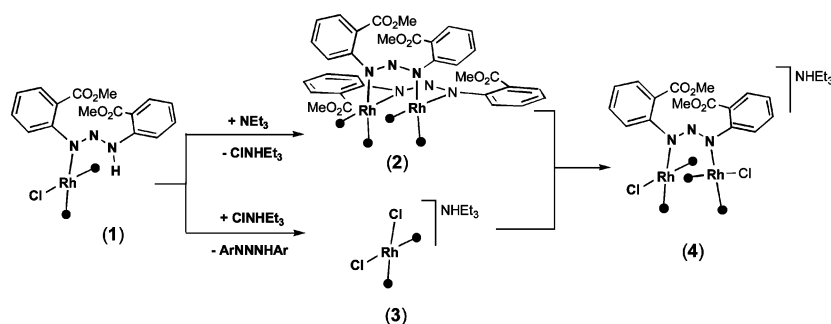
(30) Barkley, J. V.; Heaton, B. T.; Jacob, C.; Mageswaran, R.; Sampanthar, J. T. *J. Chem. Soc., Dalton Trans.* **1998**, 697.

(31) Elduque, A.; Garcés, Y.; Lahoz, F. J.; López, J. A.; Oro, L. A.; Pinillos, T.; Tejel, C. *Inorg. Chem. Commun.* **1999**, 2, 414.

**Table 2.** Selected Bond Distances (Å) and Angles (deg) for the Compound (NHET<sub>3</sub>)[Rh<sub>2</sub>(μ-ArNNNAr)Cl<sub>2</sub>(CO)<sub>4</sub>] (**4**)<sup>a</sup>

Rh(1)–Cl(1)	2.3529(16)	2.3507(16)	Rh(2)–Cl(2)	2.3489(16)	2.3401(17)
Rh(1)–N(1)	2.094(5)	2.096(5)	Rh(2)–N(3)	2.099(5)	2.105(5)
Rh(1)–C(17)	1.847(7)	1.844(7)	Rh(2)–C(19)	1.858(7)	1.863(7)
Rh(1)–C(18)	1.859(7)	1.848(7)	Rh(2)–C(20)	1.840(7)	1.842(7)
C(17)–O(5)	1.125(7)	1.130(7)	C(19)–O(7)	1.123(7)	1.129(8)
C(18)–O(6)	1.124(8)	1.140(7)	C(20)–O(8)	1.143(7)	1.140(7)
N(1)–N(2)	1.308(6)	1.297(6)	N(2)–N(3)	1.293(7)	1.294(7)
N(1)–C(8)	1.413(7)	1.426(7)	N(3)–C(9)	1.421(7)	1.430(7)
C(1)–O(1)	1.209(7)	1.207(7)	C(15)–O(3)	1.197(8)	1.192(7)
Cl(1)–Rh(1)–N(1)	90.80(14)	90.31(14)	Cl(2)–Rh(2)–N(3)	90.11(14)	89.95(14)
Cl(1)–Rh(1)–C(17)	173.01(19)	173.3(2)	Cl(2)–Rh(2)–C(19)	174.10(19)	173.8(2)
Cl(1)–Rh(1)–C(18)	88.9(2)	89.6(2)	Cl(2)–Rh(2)–C(20)	88.4(2)	88.6(2)
N(1)–Rh(1)–C(17)	89.6(2)	89.9(2)	N(3)–Rh(2)–C(19)	90.4(2)	91.0(2)
N(1)–Rh(1)–C(18)	175.7(2)	175.3(2)	N(3)–Rh(2)–C(20)	172.6(2)	174.0(2)
C(17)–Rh(1)–C(18)	90.1(3)	89.6(3)	C(19)–Rh(2)–C(20)	90.3(3)	89.8(3)
Rh(1)–N(1)–N(2)	126.3(4)	126.1(4)	Rh(2)–N(3)–N(2)	125.9(4)	125.3(4)
Rh(1)–N(1)–C(8)	120.7(4)	121.5(4)	Rh(2)–N(3)–C(9)	121.1(4)	120.8(4)
N(2)–N(1)–C(8)	111.9(5)	111.4(5)	N(2)–N(3)–C(9)	111.2(5)	112.4(5)
N(1)–N(2)–N(3)	116.8(5)	117.1(5)			

<sup>a</sup> The two figures stated correspond to the two crystallographically independent molecules. Values consigned for the second molecule are organized according to the enantiomeric relationship existent between the two independent anions.

**Scheme 1**<sup>a</sup>

<sup>a</sup> The ● symbol denotes a CO group.

to Scheme 1. The deprotonation of the triazenide ligand in **1** caused the formation of **2** along with NHET<sub>3</sub>Cl. This ammonium salt reacted with the mononuclear **1** to give the Vallarino's-type compound (NHET<sub>3</sub>)[RhCl<sub>2</sub>(CO)<sub>2</sub>] (**3**), and finally, complex **3** reacted with the dinuclear **2** to give the complex **4**, insoluble in diethyl ether.

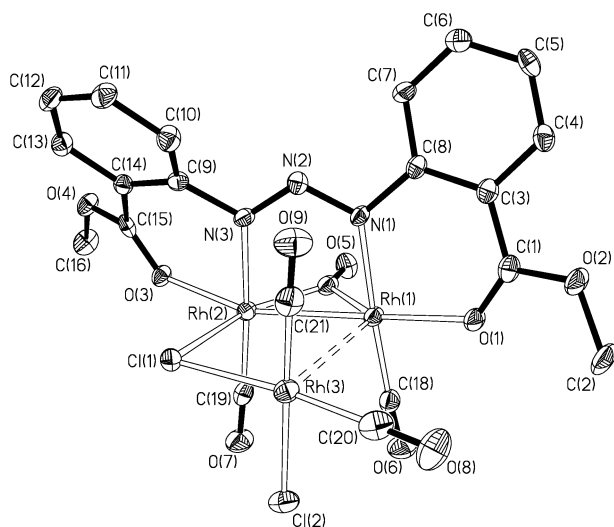
We have verified this picture with three independent experiments: (i) no changes were observed by reacting the dinuclear complex [Rh(μ-ArNNNAr)(CO)<sub>2</sub>]<sub>2</sub> (**2**) with NHET<sub>3</sub>Cl in diethyl ether; (ii) the mononuclear complex **1** evolved quantitatively to the Vallarino's-type compound **3** upon addition of NHET<sub>3</sub>Cl in diethyl ether, and more interesting, (iii) by mixing the dinuclear complex [Rh(μ-ArNNNAr)(CO)<sub>2</sub>]<sub>2</sub> (**2**) with two molar-equivalent of (NHET<sub>3</sub>)[RhCl<sub>2</sub>(CO)<sub>2</sub>] (**3**) the quantitative precipitation of **4** occurs.

This particular behavior seems to be related to the incorporation of the CO<sub>2</sub>Me groups at the *ortho* position of the phenyl groups in the triazenide ligand, since our attempts to reproduce these reactions with the triazene ligands RNNNHR (R = Ph, *p*-tolyl) were unsuccessful. Moreover, the complexes [Rh(μ-RNNNR)(CO)<sub>2</sub>]<sub>2</sub> (R = Ph, *p*-XC<sub>6</sub>H<sub>4</sub>) can be prepared cleanly by addition of NEt<sub>3</sub> to a mixture of [Rh(μ-Cl)(CO)<sub>2</sub>]<sub>2</sub> and the corresponding triazene, as previously reported.<sup>15</sup> In our particular case, the lability of the triazenide ligand in **1**, that favors the transformation of **1** into **3**, along with the facility of **2** to undergo redistribution reactions are, probably, the origin of the observed reactions.

Furthermore, the difference in the reactions of **1** with NEt<sub>3</sub> and KOH could be attributed to the low solubility in the reaction medium of the KCl formed in the second case that prevents the formation of the Vallarino's-type compound.

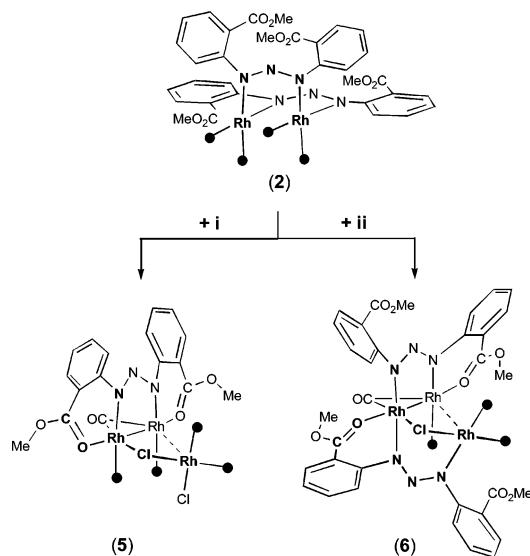
Once the ability of [Rh(μ-ArNNNAr)(CO)<sub>2</sub>]<sub>2</sub> (**2**) to undergo redistribution reactions was established, we focused our attention on the reactions of complex **2** with [Rh(μ-Cl)(CO)<sub>2</sub>]<sub>2</sub>. Addition of [Rh(μ-ArNNNAr)(CO)<sub>2</sub>]<sub>2</sub> (**2**) to [Rh(μ-Cl)(CO)<sub>2</sub>]<sub>2</sub> (1:2 molar ratio) gave a red solution from which red-violet crystals of [Rh<sub>3</sub>(μ-ArNNNAr)(μ-Cl)(μ-CO)Cl(CO)<sub>4</sub>] (**5**) (Scheme 2) deposited overnight and were characterized by X-ray diffraction methods.

The molecular structure of complex **5** is represented in Figure 2; relevant bond distances and angles are given in Table 3. The complex can be described as the result of binding of the anionic [RhCl<sub>2</sub>(CO)<sub>2</sub>]<sup>-</sup> species to the cationic dinuclear framework [Rh<sub>2</sub>(μ-ArNNNAr)(μ-CO)(CO)<sub>2</sub>]<sup>+</sup> through a highly asymmetric chloride bridge. In this framework, one bis(*o*-carboxymethylphenyl)triazene group bridges the two rhodium atoms, Rh(1) and Rh(2), through the N(1) and N(3) atoms, and chelates both metals through the oxygen atoms from the two carboxymethyl substituents (O(1) and O(3)). In this way, the bis(*o*-carboxymethylphenyl)triazene behaves as a cavity-shaped 7-electron donor ligand spanning both metal centers. In this dinuclear framework, the rhodium atoms complete a distorted square-pyramidal coordination



**Figure 2.** Molecular drawing of the trinuclear complex  $[\text{Rh}_3(\mu\text{-ArNNNAr})(\mu\text{-Cl})(\mu\text{-CO})\text{Cl}(\text{CO})_4]$  (**5**).

**Scheme 2**<sup>a</sup>



<sup>a</sup> The ● symbol denotes a CO group.

with one terminal carbonyl ligand, the second metal center, and with a bridging CO group at the apical position. The nonketonic character of bridging carbonyl was established from the observation of  $\nu(\mu\text{-CO})$  at ca.  $1845\text{ cm}^{-1}$  in the IR spectrum.

Electron counting for the cationic  $[\text{Rh}_2(\mu\text{-ArNNNAr})(\mu\text{-CO})(\text{CO})_2]^+$  fragment gave 30 v.e. and, therefore, a single metal–metal bond is required. Accordingly, the short Rh(1)–Rh(2) bond separation ( $2.5544(4)\text{ \AA}$ ) agrees with this picture. This intermetallic distance is slightly shorter than those found in the related, but neutral, complexes  $[\text{Rh}_2(\mu\text{-PPyPh}_2)_2(\mu\text{-CO})\text{Cl}_2]$  ( $2.612(1)\text{ \AA}$ )<sup>32</sup> and  $[\{\text{Rh}_2(\mu\text{-aza})(\mu\text{-CO})\text{-Cl}(\text{nbd})\}_2]$  ( $2.686(2)\text{ \AA}$ ).<sup>33</sup> The Rh(3) atom in the  $[\text{RhCl}_2(\text{CO})_2]$  moiety shows a nearly square-planar coordination with Rh(3)–Cl bond distances of  $2.3421(10)$  and  $2.3772(9)\text{ \AA}$ . The two idealized fragments are maintained together by

**Table 3.** Selected Bond Distances ( $\text{\AA}$ ) and Angles (deg) for the Trinuclear Complex  $[\text{Rh}_3(\mu\text{-ArNNNAr})(\mu\text{-Cl})(\mu\text{-CO})\text{Cl}(\text{CO})_4]$  (**5**)

Rh(1)–Rh(2)	2.5544(4)	Rh(1)···Rh(3)	3.0482(4)
Rh(1)–O(1)	2.110(2)	Rh(2)–O(3)	2.173(2)
Rh(1)–N(1)	2.048(3)	Rh(2)–N(3)	2.040(3)
Rh(1)–C(17)	2.014(4)	Rh(2)–C(17)	1.953(4)
Rh(1)–C(18)	1.860(4)	Rh(2)–C(19)	1.883(4)
C(17)–O(5)	1.166(4)	Rh(2)–Cl(1)	2.5458(9)
C(18)–O(6)	1.132(4)	C(19)–O(7)	1.131(4)
N(1)–N(2)	1.313(3)	N(2)–N(3)	1.294(4)
N(1)–C(8)	1.423(4)	N(3)–C(9)	1.435(4)
C(1)–O(1)	1.226(4)	C(15)–O(3)	1.231(4)
Rh(3)–Cl(1)	2.3772(9)	Rh(3)–Cl(2)	2.3421(10)
Rh(3)–C(20)	1.836(4)	Rh(3)–C(21)	1.829(4)
C(20)–O(8)	1.139(4)	C(21)–O(9)	1.147(4)
Rh(2)–Rh(1)–O(1)	165.51(7)	Rh(1)–Rh(2)–Cl(1)	105.12(2)
Rh(2)–Rh(1)–N(1)	85.93(7)	Rh(1)–Rh(2)–O(3)	157.78(6)
Rh(2)–Rh(1)–C(18)	95.64(11)	Rh(1)–Rh(2)–N(3)	84.43(8)
O(1)–Rh(1)–N(1)	87.58(10)	Rh(1)–Rh(2)–C(19)	98.18(10)
O(1)–Rh(1)–C(17)	143.80(12)	Cl(1)–Rh(2)–O(3)	94.74(6)
O(1)–Rh(1)–C(18)	91.76(12)	Cl(1)–Rh(2)–N(3)	85.19(8)
N(1)–Rh(1)–C(17)	88.00(12)	Cl(1)–Rh(2)–C(17)	156.10(10)
N(1)–Rh(1)–C(18)	175.75(14)	Cl(1)–Rh(2)–C(19)	91.88(11)
C(17)–Rh(1)–C(18)	90.06(14)	O(3)–Rh(2)–N(3)	87.44(10)
Rh(2)–Cl(1)–Rh(3)	85.67(3)	O(3)–Rh(2)–C(17)	108.80(12)
Rh(1)–C(17)–Rh(2)	80.14(14)	O(3)–Rh(2)–C(19)	90.92(12)
Rh(1)–C(17)–O(5)	134.5(3)	N(3)–Rh(2)–C(17)	91.61(13)
Rh(2)–C(17)–O(5)	145.3(3)	N(3)–Rh(2)–C(19)	176.52(14)
N(1)–N(2)–N(3)	116.7(3)	C(17)–Rh(2)–C(19)	91.83(15)
Rh(1)–N(1)–N(2)	124.7(2)	Rh(2)–N(3)–N(2)	127.5(2)
Rh(1)–N(1)–C(8)	125.6(2)	Rh(2)–N(3)–C(9)	121.7(2)
N(2)–N(1)–C(8)	109.6(3)	N(2)–N(3)–C(9)	110.4(3)
Cl(1)–Rh(3)–Cl(2)	89.76(3)	Cl(2)–Rh(3)–C(20)	87.36(12)
Cl(1)–Rh(3)–C(20)	173.92(12)	Cl(2)–Rh(3)–C(21)	177.39(11)
Cl(1)–Rh(3)–C(21)	91.86(11)	C(20)–Rh(3)–C(21)	90.83(16)

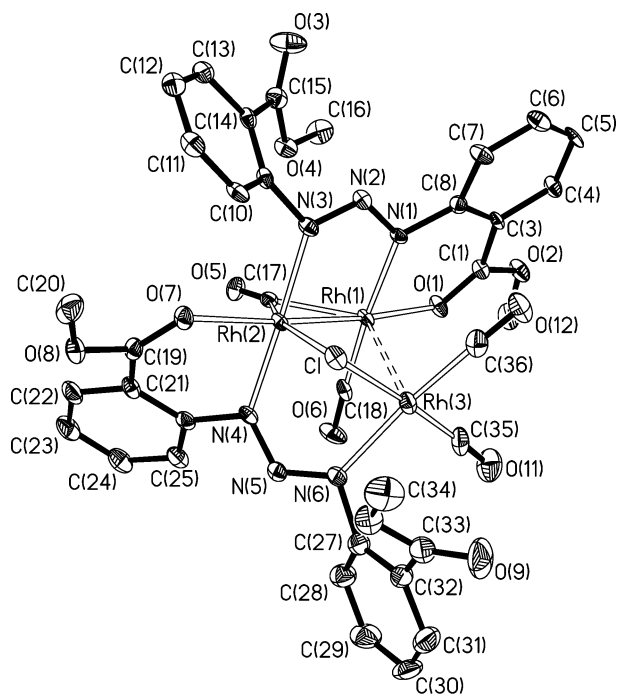
means of a Cl(1) to Rh(2) dative bond ( $2.5458(9)\text{ \AA}$ ) and, with regard to the short Rh(1)···Rh(3) separation ( $3.0482(4)\text{ \AA}$ ), a metal–metal interaction. Considering all the above commented interactions, the metal coordination spheres in the binuclear fragment can be described as distorted octahedral environments. Even in the absence of geometric constrains forcing the close proximity between Rh(3) and Rh(1), the latter interaction seems to be preferred over a second dative chloride bond from Cl(2) to Rh(1).<sup>34</sup> However, the long Rh(2)–Cl(1) bond distance and the Rh(1)···Rh(3) separation suggest that the  $[\text{RhCl}_2(\text{CO})_2]^-$  group is only weakly bound to the binuclear cationic species.

In agreement with this description, the  $[\text{RhCl}_2(\text{CO})_2]^-$  group dissociates readily in solution. Thus, complex **5** was found to be slightly conductive in acetone solutions ( $\Lambda_M = 20\text{ S cm}^2\text{ mol}^{-1}$ ), and the cationic fragment  $[\text{Rh}_2(\mu\text{-ArNNNAr})(\mu\text{-CO})(\text{CO})_2]^+$  is observed as the ion of higher  $m/z$  in the MS (FAB<sup>+</sup>) spectrum of **5**. Moreover, complex **5** is fluxional in solution, since the *o*-carboxymethylphenyl groups were found to be equivalent in the <sup>1</sup>H NMR spectrum of fresh solutions of complex **5** in CDCl<sub>3</sub> and in HDA. This fluxional behavior could be explained as due to the dissociation equilibrium of the  $[\text{RhCl}_2(\text{CO})_2]^-$  fragment, while the coordination of the CO<sub>2</sub>Me groups to the metals remains in the cationic fragment  $[\text{Rh}_2(\mu\text{-ArNNNAr})(\mu\text{-CO})(\text{CO})_2]^+$ . This binding is evident from the shift in ca.  $80\text{ cm}^{-1}$  to lower

(32) Farr, J. P.; Olmstead, M. M.; Hunt, C. H.; Balch, A. L. *Inorg. Chem.* **1981**, *20*, 1182.

(33) Oro, L. A.; Ciriano, M. A.; Villarroya, B. E.; Tiripicchio, A.; Lahoz, F. J. *J. Chem. Soc., Dalton Trans.* **1985**, 1891.

(34) A related situation stabilized only by chloride bridges has been reported for the trinuclear complex  $[\text{Rh}_3(\mu\text{-Cl})_3(\mu\text{-L})(\text{CO})_4]$  (L = bis(diphenoxyphosphino)methane). Kumar, R.; Puddhephatt, R. J.; Fronczek, F. R. *Inorg. Chem.* **1990**, *29*, 4850.



**Figure 3.** Molecular structure of the trinuclear complex  $[\text{Rh}_3(\mu\text{-ArNNNAr})_2(\mu\text{-Cl})(\mu\text{-CO})(\text{CO})_3]$  (**6**).

frequencies of the  $\nu(\text{C}=\text{O})$  bands, relative to the uncoordinated  $\text{CO}_2\text{Me}$  groups in complexes **2** and **4**, in the IR spectrum of **5** in solution.

Solutions of complex **5** in  $\text{CDCl}_3$  were found to be unstable, evolving to new compounds, whose signals in the  $^1\text{H}$  NMR spectrum start to appear in 20 min. One of them, showing four resonances for the OMe groups, was found to be the complex  $[\text{Rh}_3(\mu\text{-ArNNNAr})_2(\mu\text{-Cl})(\mu\text{-CO})(\text{CO})_3]$  (**6**) (Scheme 2). According to the formulation, complex **6** was prepared straightforwardly by reacting  $[\{\text{Rh}(\mu\text{-ArNNNAr})(\text{CO})_2\}_2]$  (**2**) and  $[\{\text{Rh}(\mu\text{-Cl})(\text{CO})_2\}_2]$  in a 1:0.5 molar ratio in hexane. From these solutions, single crystals of the brown-red complex **6** deposited in 2 days. The structure of **6** is represented in Figure 3 together with the atomic numbering scheme; the relevant bond distances and angles are given in Table 4. In complex **6** one bis(*o*-carboxymethylphenyl)triazenide bridges two rhodium atoms, Rh(1) and Rh(2), and chelates Rh(1) through the oxygen from one  $\text{CO}_2\text{Me}$  group. The other bis(*o*-carboxymethylphenyl)triazenide ligand bridges the Rh(2) and Rh(3) atoms and also chelates Rh(2) through one oxygen atom, O(7). Therefore, both triazenide groups are acting in the molecule as five electron donor ligands. This compound could be considered formally as derived from the previously described complex **5**, in which a second bis(*o*-carboxymethylphenyl)triazenide ligand was incorporated into the molecule. Thus, the  $\text{CO}_2\text{Me}$  group bonded to Rh(2), the terminal CO ligand bonded to Rh(2), and the chloride ligand coordinated to Rh(3) in **5** are replaced by one  $\text{CO}_2\text{Me}$  group and the nitrogen atoms N(4) and N(6), respectively, of the new bis(*o*-carboxymethylphenyl)triazenide ligand. This formal exchange maintains complex **6** electronically similar to **5**.

Accordingly, the bonding between Rh(1) and Rh(2) was clearly deduced from the short Rh–Rh distance (2.5538(5)

**Table 4.** Selected Bond Distances (Å) and Angles (deg) for the Trinuclear Complex  $[\text{Rh}_3(\mu\text{-ArNNNAr})_2(\mu\text{-Cl})(\mu\text{-CO})(\text{CO})_3]$  (**6**)

Rh(1)–Rh(2)	2.5538(5)	Rh(1)···Rh(3)	3.0136(5)
Rh(1)–O(1)	2.103(3)	Rh(2)–O(7)	2.243(3)
Rh(1)–N(1)	2.070(4)	Rh(2)–N(3)	2.029(4)
Rh(1)–C(17)	2.082(5)	Rh(2)–C(17)	1.895(5)
Rh(1)–C(18)	1.834(5)	Rh(2)–N(4)	2.044(4)
C(17)–O(5)	1.168(5)	Rh(2)–Cl	2.5223(12)
C(18)–O(6)	1.144(6)	C(19)–O(7)	1.228(6)
N(1)–N(2)	1.324(5)	N(4)–N(5)	1.293(5)
N(1)–C(8)	1.417(6)	N(4)–C(26)	1.423(6)
N(2)–N(3)	1.280(5)	N(5)–N(6)	1.295(5)
N(3)–C(9)	1.432(6)	N(6)–C(27)	1.442(6)
C(1)–O(1)	1.216(5)	C(19)–O(7)	1.228(6)
C(15)–O(3)	1.197(6)	C(33)–O(9)	1.200(6)
Rh(3)–Cl	2.3703(12)	Rh(3)–N(6)	2.097(4)
Rh(3)–C(35)	1.854(6)	Rh(3)–C(36)	1.862(6)
C(35)–O(11)	1.134(6)	C(36)–O(12)	1.127(6)
Rh(2)–Rh(1)–O(1)	172.00(9)	Rh(1)–Rh(2)–Cl	107.97(3)
Rh(2)–Rh(1)–N(1)	84.48(10)	Rh(1)–Rh(2)–O(7)	167.28(8)
Rh(2)–Rh(1)–C(17)	46.91(13)	Rh(1)–Rh(2)–N(3)	84.17(11)
Rh(2)–Rh(1)–C(18)	98.17(15)	Rh(1)–Rh(2)–N(4)	97.61(10)
O(1)–Rh(1)–N(1)	87.81(13)	Cl–Rh(2)–O(7)	84.74(9)
O(1)–Rh(1)–C(17)	137.11(16)	Cl–Rh(2)–N(3)	88.70(11)
O(1)–Rh(1)–C(18)	89.38(17)	Cl–Rh(2)–C(17)	161.33(14)
N(1)–Rh(1)–C(17)	99.16(16)	Cl–Rh(2)–N(4)	91.51(11)
N(1)–Rh(1)–C(18)	175.40(18)	O(7)–Rh(2)–N(3)	96.17(14)
C(17)–Rh(1)–C(18)	85.37(19)	O(7)–Rh(2)–C(17)	113.93(16)
Rh(1)–Cl–Rh(2)	78.26(3)	O(7)–Rh(2)–N(4)	81.92(14)
Rh(1)–C(17)–Rh(2)	79.74(18)	N(3)–Rh(2)–C(17)	88.97(17)
Rh(1)–C(17)–O(5)	131.0(4)	N(3)–Rh(2)–N(4)	178.05(16)
Rh(2)–C(17)–O(5)	148.8(4)	C(17)–Rh(2)–N(4)	91.45(17)
N(1)–N(2)–N(3)	116.4(4)	N(4)–N(5)–N(6)	119.5(4)
Rh(1)–N(1)–N(2)	123.0(3)	Rh(2)–N(4)–N(5)	132.6(3)
Rh(1)–N(1)–C(8)	126.7(3)	Rh(2)–N(4)–C(26)	116.3(3)
N(2)–N(1)–C(8)	110.1(4)	N(5)–N(4)–C(26)	110.9(4)
Rh(2)–N(3)–N(2)	127.1(3)	Rh(3)–N(6)–N(5)	131.1(3)
Rh(2)–N(3)–C(9)	121.6(3)	Rh(3)–N(6)–C(27)	118.7(3)
N(2)–N(3)–C(9)	111.2(4)	N(5)–N(6)–C(27)	109.1(4)
Cl–Rh(3)–N(6)	89.30(11)	N(6)–Rh(3)–C(35)	88.5(2)
Cl–Rh(3)–C(35)	176.09(16)	N(6)–Rh(3)–C(36)	173.37(19)
Cl–Rh(3)–C(36)	91.16(17)	C(35)–Rh(3)–C(36)	90.7(2)

Å). In this case, the two moieties: the dinuclear formed by Rh(1) and Rh(2), and the mononuclear “Rh(3)ClN(CO)<sub>2</sub>”, are maintained together by the 5-electron-donor bridging ligand. As described for **5**, a long dative Cl–Rh(2) bond (2.5223(12) Å), and a feeble Rh(1)···Rh(3) interaction (3.0136(5) Å) can be also proposed for **6**.

The coordination of the Rh(3) center to the second triazenide bridge ligand prevents the dissociation of this moiety in **6**. In fact, trinuclear species were observed in the MS spectrum of this compound (see Experimental Section), in contrast with the lack of trinuclear species in the MS spectrum of **5**. According to the structure found in the solid state for **6**, four inequivalent *o*- $\text{CO}_2\text{MeC}_6\text{H}_4$  groups were observed in the  $^1\text{H}$  NMR spectrum, and the coordination to the metal of one  $\text{CO}_2\text{Me}$  group per triazenide ligand was detected in the IR spectrum of **6**.

Attempts to prepare new derivatives by reacting  $[\{\text{Rh}(\mu\text{-ArNNNAr})(\text{CO})_2\}_2]$  (**2**) with  $[\{\text{Rh}(\mu\text{-Cl})(\text{CO})_2\}_2]$  in molar ratios from 1:0.5 to 1:2 led to mixtures of the complexes **5** and **6**. Finally, attempts to prepare the cationic complex  $[\text{Rh}_2(\mu\text{-ArNNNAr})(\mu\text{-CO})(\text{CO})_2]\text{PF}_6$ , proposed as a moiety in **5**, by the reaction of  $[\{\text{Rh}(\mu\text{-ArNNNAr})(\text{CO})_2\}_2]$  (**2**) with  $[\text{Rh}(\text{CO})_2(\text{MeCN})_2]\text{PF}_6$  in a 1:2 molar ratio were unsuccessful. Consequently, we believe the Rh–Cl dative bond and the Rh–Rh interaction found in complexes **5** and **6** were the

key for the stabilization of the “ $\text{Rh}_2(\mu\text{-ArNNNAr})(\mu\text{-CO})$ ” moiety.

### Concluding Remarks

The incorporation of carboxymethyl groups at the *ortho* position of the phenyl groups of the triazene PhNNNHPH ligand provides new coordination possibilities to these ligands, leading to structures with interesting features disclosed herein. Besides the typical “ $\mu\text{-}(1\kappa\text{N}^1,2\kappa\text{N}^3)$ ” coordination mode for triazenides, the bis(*o*-carboxymethylphenyl)triazene ligand is able to occupy three and four coordination positions spanning a binuclear unit. The tetradentate mode has been identified in the crescent-shaped complex  $[\text{Rh}_3(\mu\text{-ArNNNAr})(\mu\text{-Cl})(\mu\text{-CO})\text{Cl}(\text{CO})_4]$  (**5**), while the tridentate mode is found for both triazene ligands in

the complex  $[\text{Rh}_3(\mu\text{-ArNNNAr})_2(\mu\text{-Cl})(\mu\text{-CO})(\text{CO})_3]$  (**6**), where one carboxymethyl group from each ligand remains uncoordinated. To the best of our knowledge crescent-shaped complexes are quite uncommon in dinuclear rhodium(I) chemistry.

**Acknowledgment.** The financial support from Ministerio de Ciencia y Tecnología (MCyT/DGI)/FEDER) Project BQU2002-0074 is gratefully acknowledged. G.R.-M. thanks Programa CYTED for a fellowship.

**Supporting Information Available:** An X-ray crystallographic file, in CIF format, containing full details of the structural analyses of **4**, **5**, and **6**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

IC049691G