

to signals at  $\delta$  2.1 (m, 4, CH<sub>2</sub>) and 2.8 (m, 8, CH<sub>2</sub>S) assigned to DTCO,  $\delta$  2.25 (m, 4, CH<sub>2</sub>), 2.65 (m, 4, CH<sub>2</sub>S), and 3.15 (m, 4, CH<sub>2</sub>S=O) assigned to DTCS,<sup>25</sup> and  $\delta$  7.7 (m, 10, CH) assigned to BP. Benzopinacol,  $\delta$  7.2 (m, 20, CH), was prepared independently by irradiation of BP in isopropyl alcohol.

The peroxidase method<sup>50</sup> was used to determine the presence of H<sub>2</sub>O<sub>2</sub> in samples which had been irradiated in the presence of oxygen. Quantities from 1 to 200  $\mu$ L of sample were added to a 10-mL solution containing 0.1 mg of peroxidase, 3 mM leuco crystal violet, and 0.2 M acetate buffer at pH 5. The presence of H<sub>2</sub>O<sub>2</sub> causes a dark blue color to form (crystal violet). Control solutions easily detected microgram quantities of H<sub>2</sub>O<sub>2</sub> in CH<sub>3</sub>CN solutions. As an important control, the reaction of DTCO and H<sub>2</sub>O<sub>2</sub> was inspected. NMR analysis showed that addition of 30% H<sub>2</sub>O<sub>2</sub> solution (40  $\mu$ L) to 0.5 mL of 0.5 M DTCO in 80% CD<sub>3</sub>CN/D<sub>2</sub>O resulted in 50% conversion to DTCS within 60 min.

**Quantum Yield Determinations.** Quantum yields of photobleaching were determined by measuring the absorption spectrum of the sensitizer as a function of irradiation time.  $\Delta$ [Sens] was measured by determining  $\epsilon_{334}(\text{BP}) = 140$  in (80% CH<sub>3</sub>CN/H<sub>2</sub>O). The number of photons incident on the sample was determined by using a quantum counter (Rhodamine B fluorescence in ethanol) to absorb a small, constant percentage of the incident light from a 500-W mercury lamp which had passed through a monochromator. The apparatus has been previously described.<sup>49</sup> The system was calibrated by ferrioxalate actinometry. Benzophenone samples were irradiated and monitored at  $\lambda = 334$  nm. Quantum yields were obtained from the slope of a plot of  $\Delta$ [Sens] vs. einsteins absorbed and extrapolated to zero time to correct for the change in the light absorbed as the sensitizer bleached.

(50) Mottola, H. A.; Simpson, B. E.; Gorin, G. *Anal. Chem.* **1970**, *42*, 410.

Quantum yields of I<sub>3</sub><sup>-</sup> production were determined with the same quantum counting apparatus described above. Solutions containing 20 mM DTCO, 10 mM I<sup>-</sup>, and 10 mM BP in 80% CH<sub>3</sub>CN/H<sub>2</sub>O were irradiated at  $\lambda_{\text{exc}} = 334$  nm for periods of 1 to 30 min while O<sub>2</sub> was continually bubbled through a portion of the solution which was not directly irradiated. The concentration of triiodide was determined by measuring  $\Delta\text{OD}_{400}$ , a wavelength at which BP does not absorb. The molar absorptivity,  $\epsilon(\text{I}_3^-) = 3.71 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ , was determined in the same solvent system. Corrections were made for the competitive absorbance of the photoproduct, I<sub>3</sub><sup>-</sup>.

The quantum yields for sulfoxide production in the presence of oxygen were determined by monitoring the decrease in [DTCO] and the increase in [DTCS] by NMR as a function of irradiation time for samples in which [BP] = 50 mM and [DTCO] = 50 mM in 80% CD<sub>3</sub>CN/D<sub>2</sub>O ( $\lambda_{\text{exc}} = 334$  nm), with oxygen continuously bubbling through the cell during the experiment. An identical experiment was performed with 8 mM BP and 200 mM DTCO in order to monitor the photobleaching of BP after prolonged irradiation under oxygen and to calculate a turnover number (mol of BP consumed/mol of DTCS formed).

**Acknowledgment.** Support of this research by the Department of Energy, Office of Basic Energy Sciences, is gratefully acknowledged. We thank Professors W. K. Musker and R. S. Glass for helpful discussions and for providing information prior to publication and also Professors M. Z. Hoffman and K. D. Asmus for their advice and suggestions.

**Registry No.** UO<sub>2</sub><sup>2+</sup>, 16637-16-4; DTCO, 6572-95-8; benzophenone, 119-61-9; bractetyl, 431-03-8.

## Communications to the Editor

### Reactivity of Mixed Cyclometalated Palladium Compounds Containing the [2-Me<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>C(H)SiMe<sub>3</sub>] Monoanion.<sup>1</sup> Transmetalation Reaction and Formation of a Novel $\mu$ -Alkylidene Compound (X-ray) Bis( $\mu$ -chloro)bis( $\mu$ -C, $\sigma$ -N-[2-(dimethylamino)-benzylidene]( $\mu$ -chloro)(diethyl sulfide)dipalladium(II))

Fida Maassarani,<sup>2a</sup> Michel Pfeffer,<sup>\*2a</sup> Anthony L. Spek,<sup>2b</sup> Antoine M. M. Schreurs,<sup>2b</sup> and Gerard van Koten<sup>\*2c</sup>

Laboratoire de Chimie de Coordination UA 416 CNRS  
Université Louis Pasteur

F-67070 Strasbourg Cédex, France

Laboratorium voor Kristal- en Structuurchemie

University of Utrecht

3508 TB Utrecht, The Netherlands

Anorganisch Chemisch Laboratorium

University of Amsterdam, Nieuwe Achtergracht 166

1018 WV Amsterdam, The Netherlands

Received January 3, 1986

The chemistry of metal complexes containing  $\mu$ -methylene (or  $\mu$ -alkylidene) bridges is a rapidly growing field<sup>3a</sup> with the number of possible synthetic routes to these complexes still increasing.<sup>3b</sup> It was found that in order to get stable Pd<sub>2</sub>- and Pt<sub>2</sub>- $\mu$ -methylene compounds the absence of a stabilizing metal-to-metal bond had to be compensated for by the use of bridging R<sub>2</sub>PCH<sub>2</sub>PR<sub>2</sub> ligands.<sup>4,5</sup>

(1) Part 2. For part 1, see: Maassarani, F.; Pfeffer, M.; Le Borgne, G.; Wehman, E.; van Koten, G. *J. Am. Chem. Soc.* **1984**, *106*, 8002.

(2) (a) Strasbourg, France. (b) Utrecht, The Netherlands. (c) Amsterdam, The Netherlands.

(3) (a) Herrmann, W. A. *Adv. Organomet. Chem.* **1982**, *20*, 159. Pinhas, A. R.; Albright, T. A.; Hofmann, P.; Hoffmann, R. *Helv. Chim. Acta* **1980**, *63*, 29. (b) Cf. Figure 9, in: Herrmann, W. A. *J. Organomet. Chem.* **1983**, *250*, 319.

The study reported here involves reactions of mixed cyclometalated compounds Pd[2-Me<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>CH(SiMe<sub>3</sub>)](dmdba) (**1**, dmdba is 2-Me<sub>2</sub>NCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>) with PdCl<sub>2</sub>(SR<sub>2</sub>)<sub>2</sub>. Depending on the nature of the SR<sub>2</sub> ligand these reactions provide either transmetalation products or a novel type of dimeric  $\mu$ -alkylidene dipalladium compound {Pd<sub>2</sub>( $\mu$ -Cl)( $\mu'$ -Cl)(SEt<sub>2</sub>)-[(CHC<sub>6</sub>H<sub>4</sub>NMe<sub>2</sub>-2)]<sub>2</sub> (**2**). Interesting features of these reactions are (i) the novel way in forming the alkylidene fragment which involves overall 1,2-Me<sub>3</sub>SiCl elimination, (ii) the stability of the  $\mu$ -alkylidene compound **2** in which specific bridging ligands (see above) are absent, and (iii) the influence of the coligand SR<sub>2</sub> on the reaction course.

Reaction of **1**<sup>6a</sup> with *trans*-PdCl<sub>2</sub>(SEt<sub>2</sub>)<sub>2</sub><sup>6b</sup> (1:1 molar ratio) in boiling CHCl<sub>3</sub> or toluene afforded in addition to PdCl(dmdba)-(SEt<sub>2</sub>) and [PdCl(dmdba)]<sub>2</sub> (30% yield calculated on dmdba) a red crystalline product **2**, which was isolated from the reaction mixture in 26% yield (recrystallization from CH<sub>2</sub>Cl<sub>2</sub>/pentane). FD mass spectrometry, elemental analytical, and <sup>1</sup>H and <sup>13</sup>C NMR spectrometric<sup>7</sup> data indicated a Pd<sub>2</sub>Cl<sub>2</sub>(SEt<sub>2</sub>)[(C(H)C<sub>6</sub>H<sub>4</sub>NMe<sub>2</sub>-2)]

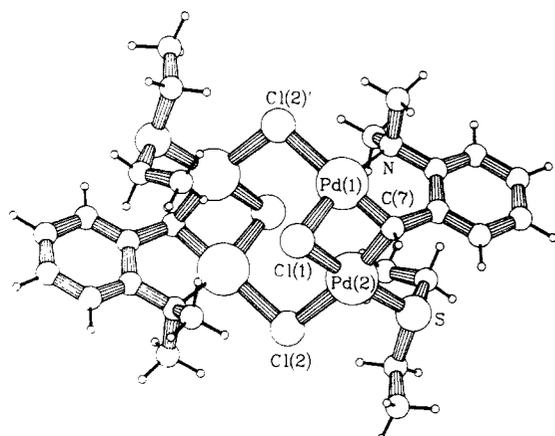
(4) Brown, M. P.; Fisher, J. R.; Puddephatt, R. J.; Seddon, K. R. *Inorg. Chem.* **1979**, *18*, 2808. Balch, A. L.; Hunt, C. T.; Lee, C.-L.; Olmstead, M. M.; Farr, J. P. *J. Am. Chem. Soc.* **1981**, *103*, 3764.

(5) Arnould, D. P.; Bennett, M. A.; McLaughlin, G. M.; Robertson, G. B.; Whittaker, M. J. *J. Chem. Soc., Chem. Commun.* **1983**, 32 and 34.

(6) (a) Maassarani, F.; Pfeffer, M.; Le Borgne, G.; van Koten, G.; Jastrzebski, J. T. B. H., manuscript in preparation. (b) With *trans*-PdCl<sub>2</sub>(SPr<sub>2</sub>)<sub>2</sub> the corresponding  $\mu$ -benzylidene compound {Pd<sub>2</sub>( $\mu$ -Cl)( $\mu'$ -Cl)(SPr<sub>2</sub>)-[(CHC<sub>6</sub>H<sub>4</sub>NMe<sub>2</sub>-2)]<sub>2</sub> is formed.

(7) <sup>1</sup>H NMR of **2** (CDCl<sub>3</sub>, Me<sub>4</sub>Si internal):  $\delta$  NMe<sub>2</sub> 3.03, 3.44 and 3.06, 3.44; CH 5.96 and 5.94; SCH<sub>2</sub> 2.3 m; CH<sub>3</sub> 1.24 (mole ratio diastereomers 3:2). <sup>13</sup>C NMR (CDCl<sub>3</sub>, Me<sub>4</sub>Si internal):  $\delta$  NMe<sub>2</sub> 53.7 and 53.3; CH 76.7; SCH<sub>2</sub> 30.7; CH<sub>3</sub> 13.2.

(8) The structure was solved by Patterson and Fourier methods (SHELX 84) and refined (SHELX 76) with anisotropic thermal parameters of the non-hydrogen atoms to  $R = 0.042$ ,  $R_w = 0.0497$ ,  $w = 1$ . Hydrogen atoms were introduced on calculated positions. A disorder model was used to include CH<sub>2</sub>Cl<sub>2</sub> molecules on 0,0,0 and 0,0,<sup>1</sup>/<sub>2</sub> positions. Full details will be given elsewhere.



**Figure 1.** Molecular structure of **2**. Some relevant bond lengths (Å): Pd(1)–C(7) 1.94 (2), Pd(2)–C(7) 2.02 (2), Pd(1)–Cl(1) 2.328 (5), Pd(2)–Cl(1) 2.496 (4), Pd(1)–Cl(2') 2.492 (5), Pd(2)–Cl(2) 2.480 (5), Pd(1)···Pd(2) 2.780 (2), C(6)–C(7) 1.49 (2), Pd(1)–N 2.09 (1), Pd(2)–S 2.293 (4). Some relevant bond angles (deg): Cl(1)–Pd(1)–Cl(2) 96.4 (2), Cl(1)–Pd(1)–N 167.6 (4), Cl(1)–Pd(1)–C(7) 84.2 (4), Cl(2')–Pd(1)–C(7) 178.7 (5), Pd(1)–Cl(1)–Pd(2) 70.3 (1), Pd(1)–C(7)–Pd(2) 89.1 (7), Pd(1)–C(7)–C(6) 113 (1), Pd(1)–N–C(1) 109 (1), Cl(2')–Pd(1)–N 94.7 (4), N–Pd(1)–C(7) 84.8 (6), Pd(2)–C(7)–C(6) 123 (1), C(7)–Pd(2)–S 93.6 (4), C(7)–Pd(2)–Cl(2) 167.3 (4), Cl(1)–Pd(2)–S 167.9 (2), Cl(1)–Pd(2)–Cl(2) 90.6 (2). Atoms related by inversion symmetry have been dashed.

stoichiometry, i.e., the isolation of a product in which the SiMe<sub>3</sub> grouping was no longer present.

The preliminary data of an X-ray diffraction analysis<sup>8</sup> of **2** established the above stoichiometry and showed this compound to be a novel type of  $\mu$ -alkylidene metal complex. Crystal data (C<sub>13</sub>H<sub>21</sub>Cl<sub>2</sub>NPd<sub>2</sub>S)<sub>2</sub>·<sup>2</sup>/<sub>3</sub>CH<sub>2</sub>Cl<sub>2</sub>; trigonal space group *R* $\bar{3}$ , *a* = *b* = 20.485 (4) Å, *c* = 22.951 (2) Å, *U* = 8341 (2), *Z* = 9, *D*<sub>c</sub> = 1.918 g cm<sup>-3</sup>,  $\mu$ (Mo K $\alpha$ ) = 23.8 cm<sup>-1</sup>, 1550 observed [*I*  $\geq$  2.5 $\sigma$ (*I*)] intensities (Enraf-Nonius CAD4F diffractometer) with  $\theta \leq 22^\circ$  ( $\omega/2\theta$  scan).

The dimeric molecule (Figure 1), which has inversion symmetry, contains two dinuclear  $\mu$ -benzylidene units bridged by Cl atoms of different units thus forming an almost planar Pd<sub>2</sub>( $\mu$ -Cl)<sub>2</sub>Pd<sub>2</sub> arrangement. The dinuclear unit consists of two approximately planar coordinated Pd atoms (angle between these planes is 65.8 (3)°) which are unsymmetrically bridged (vide infra) by both the benzylidene C atom, C(7), and one Cl atom, Cl(1). The Pd(1)–C(7)–Pd(2) angle amounts to 89.1 (7)° which is a typical value for the internal angle at a  $\mu$ -CHR bonded C-atom<sup>3</sup> (C–H 1.06 (2) Å, the benzylidene H atom was located).

The <sup>1</sup>H and <sup>13</sup>C NMR data for C(7)H, 5.95 and 76.7 ppm, respectively, are consistent with these values expected for a  $\mu$ -alkylidene group lacking a Pd–Pd bond.<sup>9</sup> It is therefore interesting to observe that the Pd(1)···Pd(2) distance is surprisingly short (2.780 (2) Å) when compared to these distances in other Cl-bridged Pd<sub>2</sub> complexes in which the Pd···Pd separation is usually  $\geq$  3.20 Å.<sup>10</sup> This short Pd···Pd distance in **2** may arise from the different ligand surroundings of Pd(1) and Pd(2) which give rise to different electron densities at these Pd atoms.<sup>12</sup> This may lead

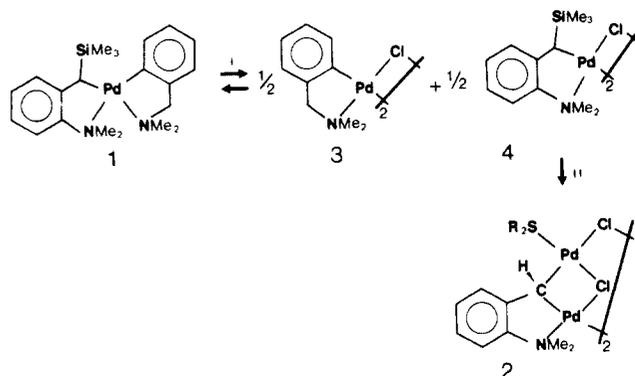
(9) This tetranuclear structure of **2** is retained in solution. <sup>1</sup>H NMR data show by the diastereotopism of the NMe<sub>2</sub> grouping that the  $\mu$ -benzylidene C atom is a stable chiral center, while the fact that two resonance patterns are observed in <sup>1</sup>H NMR spectrum (see ref 7) point to the formation of two diastereomeric pairs (*SS/RR* and *SR/RS*).

(10) See, for instance: Barr, N.; Dyke, S. F.; Smith, G.; Kennard, C. H. L.; McKee, V. *J. Organomet. Chem.* **1985**, *288*, 109. Pfeffer, M.; Fischer, J.; Mitschler, A. *Organometallics* **1984**, *3*, 1531. Braunstein, P.; Matt, D.; Dusausy, Y.; Fischer, J.; Mitschler, A.; Ricard, L. *J. Am. Chem. Soc.* **1981**, *103*, 5115.

(11) Note, however, that in *cis*-Pd(NH<sub>2</sub>CH(COOH)CH<sub>2</sub>CH<sub>2</sub>SiMe<sub>3</sub>)Cl<sub>2</sub> the two Pd–Cl bonds are nearly equal: Warren, R. C.; McConnell, J. F.; Stephenson, N. C. *Acta Crystallogr., Sect. B* **1970**, *B26*, 1402.

(12) A comparable situation has been met in the structure of [(*dmba*)Pd- $\mu$ -C(CF<sub>3</sub>)=C(CF<sub>3</sub>)C(CF<sub>3</sub>)=C(CF<sub>3</sub>)Pd(5)] with a Pd···Pd of 2.756 (1) Å.<sup>1</sup>

**Scheme 1'**

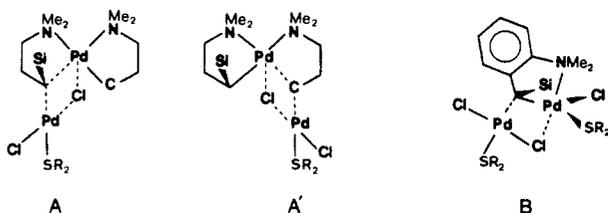


<sup>a</sup> (i) Boiling CH<sub>2</sub>Cl<sub>2</sub> or toluene, *trans*-PdCl<sub>2</sub>(SR<sub>2</sub>)<sub>2</sub>, R = Me, primary or secondary alkyl. (ii) Boiling CH<sub>2</sub>Cl<sub>2</sub> or toluene, *trans*-PdCl<sub>2</sub>(SR<sub>2</sub>)<sub>2</sub>, R = primary alkyl.

to a bonding scheme involving a [(Et<sub>2</sub>S)Cl(2)Pd(2)]<sup>+</sup> unit which is  $\sigma$  bonded to a planar, 4- $e$ -donating { $[\mu$ -Cl(1)]Pd(1)C(7)}<sup>-</sup> unit via Cl(1) and C(7). The significantly shorter bridge bond of Cl(1) to Pd(1) than to Pd(2) may reflect either a stronger trans effect of the SEt<sub>2</sub> ligand compared to the NMe<sub>2</sub> grouping of **5**<sup>11</sup> (**5** is CH(SiMe<sub>3</sub>)C<sub>6</sub>H<sub>4</sub>NMe<sub>2</sub>-2 anion) or that localized covalent Cl(1)–Pd(1) and donative Cl(1)–Pd(2) bonds are present in this molecule. The angle at C(7) between C(6) and Pd(2) (123 (1)°) deviates much from the tetrahedral value for a sp<sup>3</sup> hybridized C atom in contrast to the normal angle of 113 (1)° found with Pd(1). This may arise from the fact that C(7) is part of a five-atom chelate ring (cf. the relatively large<sup>13</sup> bite angle of 84.8 (6)°).

Various observations indicate that the formation of **2** is connected to the transmetalation reactions of **1** with *trans*-PdCl<sub>2</sub>(SR<sub>2</sub>)<sub>2</sub> because when R = Me or sec-alkyl exclusively the transmetalation products Pd(*dmba*)Cl (**3**)<sup>14</sup> and Pd[CH-(SiMe<sub>3</sub>)C<sub>6</sub>H<sub>4</sub>NMe<sub>2</sub>-2]Cl (**4**)<sup>14</sup> are obtained, see Scheme I. The result of separate experiments confirmed the occurrence of steps i and ii: i.e., the 1:1 molar reaction of **4** with PdCl<sub>2</sub>(SEt<sub>2</sub>)<sub>2</sub> afforded **2** quantitatively, while moreover, the yield of isolated **2** increased to 43% in the 1:2 molar reaction of **1** with PdCl<sub>2</sub>(SEt<sub>2</sub>)<sub>2</sub>.

A and A' (see Scheme I) are possible intermediates in the



transmetalation step, which involves electrophilic attack of a (R<sub>2</sub>S)Cl<sub>2</sub>Pd entity on the benzylic (or aromatic, A')<sup>15</sup> carbon atom, an attack which is assisted by the formation of a  $\mu$ -Cl bridge. A possible rationale for the formation of the  $\mu$ -benzylidene compound **2** is attack of (Et<sub>2</sub>S)Cl<sub>2</sub>Pd<sup>16a</sup> on the benzylic carbon atom in **4**, which must occur from the side opposite to the SiMe<sub>3</sub> group.<sup>17</sup> Movement of the NMe<sub>2</sub> ligand *trans* to the attacking Cl atom

(13) Generally such bite angles are in the range of 76–83°.<sup>10,17</sup>

(14) As the monomer with a coordinated SR<sub>2</sub> ligand or the Cl-bridged dimer. The latter product is present exclusively when the reaction mixture is worked up.

(15) In both cases the same transmetalation products are formed.

(16) (a) Or (Pr<sub>2</sub>S)Cl<sub>2</sub>Pd in the case of the formation of {Pd<sub>2</sub>( $\mu$ -Cl)( $\mu'$ -Cl)(SPR<sub>2</sub>)[(C(H)C<sub>6</sub>H<sub>4</sub>NMe<sub>2</sub>-2)]<sub>2</sub>}<sub>2</sub>.<sup>6b</sup> (b) In such an intermediate both Me<sub>3</sub>Si and one Cl are at the same side of the cyclometalated ring in particular when the Pd center is five-coordinate.

(17) In the five-membered chelate ring MCH(SiMe<sub>3</sub>)C<sub>6</sub>H<sub>4</sub>NMe<sub>2</sub>-2 the bulky SiMe<sub>3</sub> group is in axial position thus screening effectively one side of the metallocycle from attack, cf. the structures of SnMePhBr(**5**),<sup>17b</sup> Pd(**5**)[C<sub>6</sub>H<sub>4</sub>CH(Me)NMe<sub>2</sub>-2-(S)]<sub>2</sub>,<sup>6a</sup> and PtCl(**5**)(SEt<sub>2</sub>).<sup>17c</sup> (b) Jastrzebski, J. T. B. H.; van Koten, G.; Knaap, C. T.; Schreurs, A. M. M.; Kroon, J.; Spek, A. L. *Organometallics*, in print. (c) An X-ray structure confirmed the *cis* arrangement of the NMe<sub>2</sub> and Cl ligands: Wehman, E. Ph.D. Thesis, 1986, Amsterdam.

then provides intermediate B (Scheme I) from which  $\text{Me}_3\text{Si}^+$  and  $\text{Cl}^-$  can easily eliminate<sup>16b</sup> to form 2.

The mechanistic details of these reactions comprising particularly the crucial role of the  $\text{R}_2\text{S}$  coligand are investigated currently because, when understood,<sup>18</sup> this synthetic route may provide an interesting new entry into the synthesis of new types of  $\mu$ -alkylidene-Pd compounds.

**Acknowledgment.** Dr. A. J. M. Duisenberg is thanked for the data collection of 2. These investigations were supported in part by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for the Advancement of Pure Research (ZWO) (to A.L.S.). The CNRS is thanked for financial support (to G.v.K. and F.M.).

**Supplementary Material Available:** Final values of refined positional and thermal parameters and an ORTEP view of 2 (40% probability) (2 pages). Ordering information is given on any current masthead page.

(18) In intermediate B the  $\text{SR}_2$  group must be present because of the influence this coligand exerts on the product formation (see Scheme I).

### Formation of Fe-Os, Fe-Ru, and Fe-Co Bimetallic Particles by Thermal Decomposition of Heteropolynuclear Clusters Supported on a Partially Dehydroxylated Magnesia

A. Choplin,\* L. Huang, A. Theolier, P. Gallezot, and J. M. Basset\*

*Institut de Recherches sur la Catalyse  
Conventionné à l'Université Claude Bernard  
Lyon I, 69626 Villeurbanne Cédex, France*

U. Siriwardane and S. G. Shore\*

*Department of Chemistry, The Ohio State University  
Columbus, Ohio 43210*

R. Mathieu

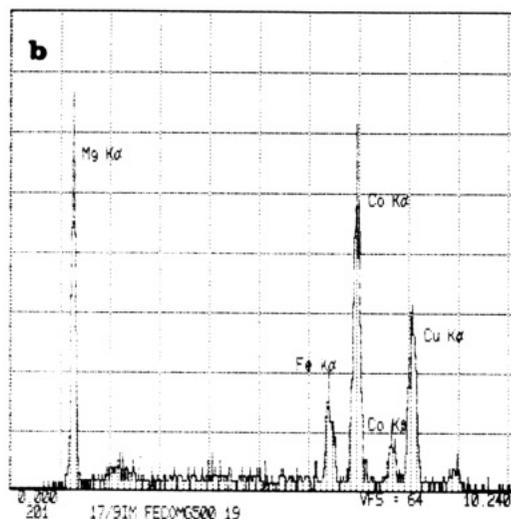
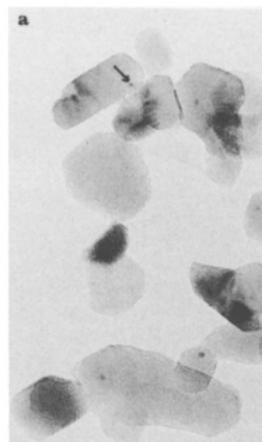
*Laboratoire de Chimie de Coordination du CNRS  
Associé à l'Université Paul Sabatier  
31400 Toulouse, France*

Received December 12, 1985

Bimetallic systems represent an important class of heterogeneous catalysts.<sup>1,2</sup> So far, most of the methods of preparation were mainly based on coimpregnation, ion-exchange, or coprecipitation techniques, which require high-temperature reduction of two metal salts adsorbed on an oxide support.

Recently, heteropolynuclear molecular clusters have been used as precursors of hypothetical bimetallic particles, which exhibited, in some cases, unusual catalytic properties in various kinds of reactions.<sup>3-12</sup> However, interpretation of the results was made

- (1) Sinfelt, J. H. *J. Catal.* **1973**, *29*, 308-315.
- (2) Clarke, J. K. A.; Creaner, A. C. M. *Ind. Eng. Chem. Prod., Res. Div.* **1981**, *20*, 574-593.
- (3) Ichikawa, M. *J. Catal.* **1979**, *59*, 67-78.
- (4) Anderson, J. R.; Elmes, P. S.; Howe, R. F.; Mainwaring, D. E. *J. Catal.* **1977**, *50*, 508-518.
- (5) Choplin, A.; Leconte, M.; Basset, J. M.; Hsu, W. L.; Shore, S. G. *J. Mol. Catal.* **1983**, *21*, 389-391.
- (6) Moggi, P.; Albanesi, G.; Predieri, G.; Sappa, E. *J. Organomet. Chem.* **1983**, *252*, C89-C92.
- (7) Hemmerich, R.; Keim, W.; Röper, M. *J. Chem. Soc., Chem. Commun.* **1983**, 428-430.
- (8) Vanhove, D.; Makambo, L.; Blanchard, M. *J. Chem. Res., Synop.* **1980**, 335; *J. Chem. Res.* **1980**, 4121-4132.
- (9) Shapley, J. R.; Hardwick, S. J.; Foose, D. S.; Stucky, G. D.; Churchill, M. R.; Bueno, Cl.; Hutchinson, J. P. *J. Am. Chem. Soc.* **1981**, *103*, 7383-7385.



**Figure 1.** Fe-Co cluster issued from the decomposition of  $\text{HFeCo}_3(\text{CO})_{12}/\text{MgO}$  at 500 °C under  $\text{H}_2$ : (a) TEM view of Fe-Co/MgO (500 000 magnification); (b) EDS spectrum of a 20-Å Fe-Co cluster (arrowed on (a)), taken with a  $10 \text{ \AA} \times 10 \text{ \AA}$  analysis window in the STEM VGHB 501 equipped with a Tracor EDX analyzer. The quantitative analysis from Fe  $\text{K}\alpha$  and Co  $\text{K}\alpha$  emission peak gives a ratio  $\text{Co}/\text{Fe} = 3.0 \pm 0.4$  (Cu  $\text{K}\alpha$  peak corresponds to the copper grid supporting the sample).

difficult due to the lack of information regarding the real nature of the particles (size, surface, and bulk composition).

We wish to report here that with  $\text{H}_2\text{FeOs}_3(\text{CO})_{13}$ ,  $\text{H}_2\text{FeRu}_3(\text{CO})_{13}$ , and  $\text{HFeCo}_3(\text{CO})_{12}$  supported on a partially hydroxylated magnesia, it is possible to obtain, after  $\text{H}_2$  treatment at 400 °C, very small bimetallic particles, having the same bulk composition as that of the starting heteropolynuclear precursor cluster. This conclusion is based on high spatial resolution analytical microscopy.

The magnesia (100  $\text{m}^2/\text{g}$ ) was treated under  $\text{O}_2$  for 10 h at 400 °C, evacuated at 400 °C under vacuum ( $10^{-5}$  torr), equilibrated with  $\text{H}_2\text{O}$  (25 torr) at 25 °C for 16 h, and then evacuated at 200 °C (16 h,  $10^{-5}$  torr).

$\text{H}_2\text{FeOs}_3(\text{CO})_{13}$ ,  $\text{H}_2\text{FeRu}_3(\text{CO})_{13}$ , and  $\text{HFeCo}_3(\text{CO})_{12}$  were prepared according to known procedures.<sup>13-15</sup> The clusters were chemisorbed on magnesia from  $\text{CH}_2\text{Cl}_2$  solutions. It has been

- (10) Kuznetsov, V. L.; Danilyuk, A. F.; Kolosova, I. E.; Yermakov, Yu. I. *React. Kinet. Catal. Lett.* **1982**, *21*, 249-254.
- (11) Budge, J. R.; Lücke, B. F.; Gates, B. C.; Toran, J. J. *J. Catal.* **1985**, *91*, 272-282.
- (12) Iwasawa, Y.; Yamada, M. *J. Chem. Soc., Chem. Commun.* **1985**, 675-676.
- (13) Churchill, M. R.; Bueno, C.; Hsu, W. L.; Plotkin, J. S.; Shore, S. G. *Inorg. Chem.* **1982**, *21*, 1958-1963.
- (14) Geoffroy, G. L.; Fox, J. R.; Burkhardt, E.; Foley, H. C.; Harley, A. D.; Rosen, R. *Inorg. Synth.* **1982**, *21*, 58-66.
- (15) Chini, P.; Colli, L.; Peraldo, M. *Gazz. Chim. Ital.* **1960**, *90*, 1005-1020.