to signals at δ 2.1 (m, 4, CH_2) and 2.8 (m, 8, CH_2S) assigned to DTCO,[46c] δ 2.25 (m, 4, CH_2), 2.65 (m, 4, CH_2S), and 3.15 (m, 4, $CH_2S{=}O$) assigned to DTCS,[25] and δ 7.7 (m, 10, CH) assigned to BP. Benzpinacol, δ 7.2 (m, 20, CH), was prepared independently by irradiation of BP in isopropyl alcohol.

The peroxidase method[50] was used to determine the presence of H_2O_2 in samples which had been irradiated in the presence of oxygen. Quantities from 1 to 200 μL 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_2O_2 causes a dark blue color to form (crystal violet). Control solutions easily detected microgram quantities of H_2O_2 in CH_3CN solutions. As an important control, the reaction of DTCO and H_2O_2 was inspected. NMR analysis showed that addition of 30% H_2O_2 solution (40 μL) to 0.5 mL of 0.5 M DTCO in 80% CD_3CN/D_2O 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. Δ[Sens] was measured by determining ϵ_{334}(BP) = 140 in (80% CH_3CN/H_2O). 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.[49] The system was calibrated by ferrioxalate actinometry. Benzophenone samples were irradiated and monitored at λ = 334 nm. Quantum yields were obtained from the slope of a plot of Δ[Sens] vs. einsteins absorbed and extrapolated to zero time to correct for the change in the light absorbed as the sensitizer bleached.

Quantum yields of I_3^- production were determined with the same quantum counting apparatus described above. Solutions containing 20 mM DTCO, 10 mM I^-, and 10 mM BP in 80% CH_3CN/H_2O were irradiated at λ_{exc} = 334 nm for periods of 1 to 30 min while O_2 was continually bubbled through a portion of the solution which was not directly irradiated. The concentration of triiodide was determined by measuring ΔOD_{400}, a wavelength at which BP does not absorb. The molar absorptivity, $\epsilon(I_3^-) = 3.71 \times 10^3\ M^{-1}\ cm^{-1}$, was determined in the same solvent system. Corrections were made for the competitive absorbance of the photoproduct, I_3^-.

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_3CN/D_2O (λ_{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_2^{2+}, 16637-16-4; DTCO, 6572-95-8; benzophenone, 119-61-9; bracetyl, 431-03-8.

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Communications to the Editor

Reactivity of Mixed Cyclometalated Palladium Compounds Containing the [2-$Me_2NC_6H_4C(H)SiMe_3$] Monoanion.[1] Transmetalation Reaction and Formation of a Novel μ-Alkylidene Compound (X-ray) Bis(μ-chloro)bis{μ-*C*,σ-*N*-[2-(dimethylamino)benzylidene](μ-chloro)(diethyl sulfide)dipalladium(II)}

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The chemistry of metal complexes containing μ-methylene (or μ-alkylidene) bridges is a rapidly growing field[3a] with the number of possible synthetic routes to these complexes still increasing.[3b] It was found that in order to get stable Pd_2– and Pt_2–μ-methylene compounds the absence of a stabilizing metal-to-metal bond had to be compensated for by the use of bridging $R_2PCH_2PR_2$ ligands.[4,5]

The study reported here involves reactions of mixed cyclometalated compounds Pd[2-$Me_2NC_6H_4CH(SiMe_3)$](dmba) (**1**, dmba is 2-$Me_2NCH_2C_6H_4$) with $PdCl_2(SR_2)_2$. Depending on the nature of the SR_2 ligand these reactions provide either transmetalation products or a novel type of dimeric μ-alkylidene dipalladium compound {Pd_2(μ-Cl)(μ′-Cl)(SEt_2)-[($CHC_6H_4NMe_2$-2)]}$_2$ (**2**). Interesting features of these reactions are (i) the novel way in forming the alkylidene fragment which involves overall 1,2-Me_3SiCl elimination, (ii) the stability of the μ-alkylidene compound **2** in which specific bridging ligands (see above) are absent, and (iii) the influence of the coligand SR_2 on the reaction course.

Reaction of **1**[6a] with *trans*-$PdCl_2(SEt_2)_2$[6b] (1:1 molar ratio) in boiling $CHCl_3$ or toluene afforded in addition to PdCl(dmba)(SEt_2) and [PdCl(dmba)]$_2$ (30% yield calculated on dmba) a red crystalline product **2**, which was isolated from the reaction mixture in 26% yield (recrystallization from CH_2Cl_2/pentane). FD mass spectrometry, elemental analytical, and ^1H and ^{13}C NMR spectrometric[7] data indicated a $Pd_2Cl_2(SEt_2)[(C(H)C_6H_4NMe_2\text{-}2)]$

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[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.

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[6] (a) Maassarani, F.; Pfeffer, M.; Le Borgne, G.; van Koten, G.; Jastrzebski, J. T. B. H., manuscript in preparation. (b) With *trans*-$PdCl_2(SPr_2)_2$ the corresponding μ-benzylidene compound {Pd_2(μ-Cl)(μ′-Cl)(SPr_2)-[($CHC_6H_4NMe_2$-2)]}$_2$ is formed.

[7] ^1H NMR of **2** ($CDCl_3$, Me_4Si internal): δ NMe_2 3.03, 3.44 and 3.06, 3.44; CH 5.96 and 5.94; SCH_2 2.3 m; CH_3 1.24 (mole ratio diastereomers 3:2). ^{13}C NMR ($CDCl_3$, Me_4Si internal): δ NMe_2 53.7 and 53.3; CH 76.7; SCH_2 30.7; CH_3 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 $R = 0.042$, $R_{wF} = 0.0497$, $w = 1$. Hydrogen atoms were introduced on calculated positions. A disorder model was used to include CH_2Cl_2 molecules on 0,0,0 and 0,0,$^1/_2$ positions. Full details will be given elsewhere.

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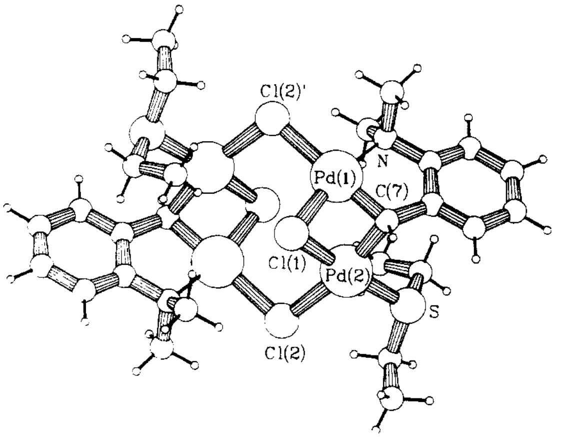


Figure 1. Molecular structure of **2**. Some relevant bond lengths (Å): Pd(1)–C(7) 1.94 (2), Pd(2)–C(7) 2.02 (2), Pd(1)–Cl(1) 2.328 (5), Pd(2)–Cl(1) 2.496 (4), Pd(1)–Cl(2′) 2.492 (5), Pd(2)–Cl(2) 2.480 (5), Pd(1)··Pd(2) 2.780 (2), C(6)–C(7) 1.49 (2), Pd(1)–N 2.09 (1), Pd(2)–S 2.293 (4). Some relevant 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.

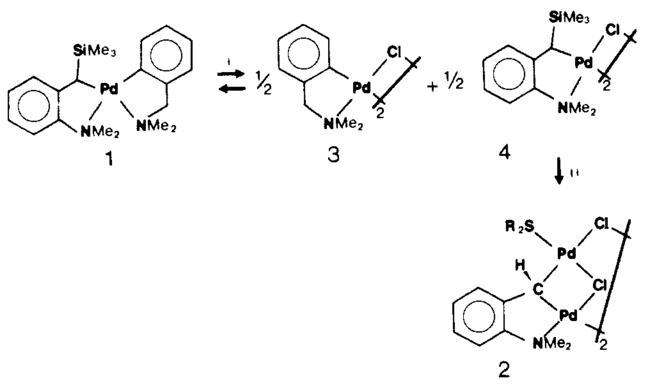
stoichiometry, i.e., the isolation of a product in which the $SiMe_3$ grouping was no longer present.

The preliminary data of an X-ray diffraction analysis[8] of **2** established the above stoichiometry and showed this compound to be a novel type of μ-alkylidene metal complex. Crystal data $(C_{13}H_{21}Cl_2NPd_2S)_2 \cdot {}^2/_3CH_2Cl_2$: trigonal space group $R\bar{3}$, $a = b = 20.485$ (4) Å, $c = 22.951$ (2) Å, $U = 8341$ (2), $Z = 9$, $D_c = 1.918$ g cm^{-3}, μ(Mo Kα) = 23.8 cm^{-1}, 1550 observed [$I \geq 2.5\sigma(I)$] intensities (Enraf-Nonius CAD4F diffractometer) with $\theta \leq 22°$ ($\omega/2\theta$ scan).

The dimeric molecule (Figure 1), which has inversion symmetry, contains two dinuclear μ-benzylidene units bridged by Cl atoms of different units thus forming an almost planar $Pd_2(\mu\text{-}Cl)_2Pd_2$ 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 μ-CHR bonded C-atom[3] (C–H 1.06 (2) Å, the benzylidene H atom was located).

The ^1H and ^{13}C NMR data for C(7)H, 5.95 and 76.7 ppm, respectively, are consistent with these values expected for a μ-alkylidene group lacking a Pd–Pd bond.[9] 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_2 complexes in which the Pd···Pd separation is usually ≥3.20 Å.[10] 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.[12] This may lead to a bonding scheme involving a $[(Et_2S)Cl(2)Pd(2)]^+$ unit which is σ bonded to a planar, 4-e-donating $\{[\mu\text{-}Cl(1)]Pd(1)C(7)\}^-$ 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_2 ligand compared to the NMe_2 grouping of **5**[11] (**5** is $CH(SiMe_3)C_6H_4NMe_2$-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^3 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[13] bite angle of 84.8 (6)°).

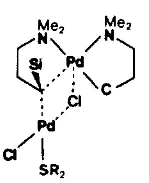
Scheme I[a]



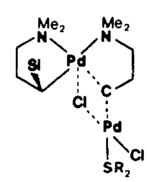
[a] (i) Boiling CH_2Cl_2 or toluene, *tr*-$PdCl_2(SR_2)_2$, R = Me, primary or secondary alkyl. (ii) Boiling CH_2Cl_2 or toluene, *tr*-$PdCl_2(SR_2)_2$, R = primary alkyl.

Various observations indicate that the formation of **2** is connected to the transmetalation reactions of **1** with *trans*-$PdCl_2(SR_2)_2$ because when R = Me or sec-alkyl exclusively the transmetalation products Pd(dmba)Cl (**3**)[14] and Pd[$CH(SiMe_3)C_6H_4NMe_2$-2]Cl (**4**)[14] 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 $PdCl_2(SEt_2)_2$ afforded **2** quantitatively, while moreover, the yield of isolated **2** increased to 43% in the 1:2 molar reaction of **1** with $PdCl_2(SEt_2)_2$.

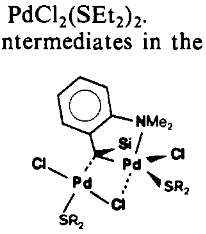
A and A′ (see Scheme I) are possible intermediates in the



A



A′



B

transmetalation step, which involves electrophilic attack of a $(R_2S)Cl_2Pd$ entity on the benzylic (or aromatic, A′)[15] carbon atom, an attack which is assisted by the formation of a μ-Cl bridge. A possible rationale for the formation of the μ-benzylidene compound **2** is attack of $(Et_2S)Cl_2Pd$[16a] on the benzylic carbon atom in **4**, which must occur from the side opposite to the $SiMe_3$ group.[17] Movement of the NMe_2 ligand trans to the attacking Cl atom

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(9) This tetranuclear structure of **2** is retained in solution. ^1H NMR data show by the diastereotopism of the NMe_2 grouping that the μ-benzylidene C atom is a stable chiral center, while the fact that two resonance patterns are observed in ^1H NMR spectrum (see ref 7) point to the formation of two diastereomeric pairs (*SS*/*RR* and *SR*/*RS*).

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(11) Note, however, that in *cis*-$\overline{Pd(NH_2CH(COOH)CH_2CH_2S}Me)Cl_2$ 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-μ-{$C(CF_3)=C(CF_3)C(CF_3)=C(CF_3)$}Pd(**5**)] with a Pd···Pd of 2.756 (1) Å.[1]

(13) Generally such bite angles are in the range of 76–83°.[10,17]

(14) As the monomer with a coordinated SR_2 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 $(Pr_2S)Cl_2Pd$ in the case of the formation of $\{Pd_2(\mu\text{-}Cl)(\mu'\text{-}Cl)(SPr_2)[(C(H)C_6H_4NMe_2\text{-}2)]\}_2$.[6b] (b) In such an intermediate both Me_3Si 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 $\overline{MCH(SiMe_3)C_6H_4N}Me_2$-2 the bulky $SiMe_3$ group is in axial position thus screening effectively one side of the metallocycle from attack, cf. the structures of SnMePhBr(**5**),[17b] Pd(**5**)[$C_6H_4CH(Me)NMe_2$-2-(*S*)],[6a], and PtCl(**5**)(SEt_2).[17c] (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_2 and Cl ligands: Wehman, E. Ph.D. Thesis, 1986, Amsterdam.

then provides intermediate B (Scheme I) from which Me_3Si^+ and Cl^- can easily eliminate[16b] to form **2**.

The mechanistic details of these reactions comprising particularly the crucial role of the R_2S coligand are investigated currently because, when understood,[18] this synthetic route may provide an interesting new entry into the synthesis of new types of μ-alkylidene–Pd compounds.

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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.

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[18] In intermediate B the 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

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Bimetallic systems represent an important class of heterogeneous catalysts.[1,2] 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.[3-12] However, interpretation of the results was made difficult due to the lack of information regarding the real nature of the particles (size, surface, and bulk composition).

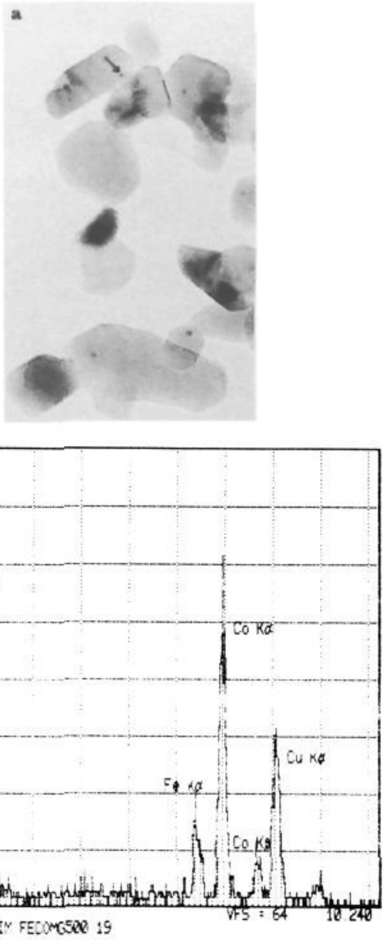

Figure 1. Fe–Co cluster issued from the decomposition of $HFeCo_3(CO)_{12}/MgO$ at 500 °C under H_2: (a) TEM view of Fe–Co/MgO (500 000 magnification); (b) EDS spectrum of a 20-Å Fe–Co cluster (arrowed on (a)), taken with a 10 Å × 10 Å analysis window in the STEM VGHB 501 equipped with a Tracor EDX analyzer. The quantitative analysis from Fe Kα and Co Kα emission peak gives a ratio Co/Fe = 3.0 ± 0.4 (Cu Kα peak corresponds to the copper grid supporting the sample).

We wish to report here that with $H_2FeOs_3(CO)_{13}$, $H_2FeRu_3(CO)_{13}$, and $HFeCo_3(CO)_{12}$ supported on a partially hydroxylated magnesia, it is possible to obtain, after 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 m^2/g) was treated under O_2 for 10 h at 400 °C, evacuated at 400 °C under vacuum (10^{-5} torr), equilibrated with H_2O (25 torr) at 25 °C for 16 h, and then evacuated at 200 °C (16 h, 10^{-5} torr).

$H_2FeOs_3(CO)_{13}$, $H_2FeRu_3(CO)_{13}$, and $HFeCo_3(CO)_{12}$ were prepared according to known procedures.[13-15] The clusters were chemisorbed on magnesia from CH_2Cl_2 solutions. It has been

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