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Some Reactions of Dipalladium(I) and Diplatinum(I) Complexes of the Type $[M_2(\mu\text{-}SPR'_2)_2(PR_3)_2]$ (M = Pd, Pt; R, R′ = Alkyl, Aryl). Crystal and Molecular Structure of $[Pd_2(\mu\text{-}SPPh_2)_2(CNMe)_2]\cdot CHCl_3$

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Exchange of both terminal tertiary phosphine ligands of $[M_2(\mu\text{-}SPR'_2)_2(PR_3)_2]$ (M = Pd, Pt; R, R′ = alkyl, aryl) complexes readily occurs with $P(OPh)_3$, $PhP(OPh)_2$, $Ph_2PCH_2PPh_2$, and CNR″ (R″ = Me, *t*-Bu). $Ph_2PCH_2PPh_2$ acts as a monodentate ligand in the complex thus obtained. No insertion reactions into the metal–metal bond of $[M_2(\mu\text{-}SPR'_2)_2(PR_3)_2]$ are observed with CNR″, CO, S_8 or SO_2. The new complexes are characterized by means of ^1H, ^{31}P, and ^{195}Pt NMR and IR spectroscopy. The crystal and molecular structure of $[Pd_2(\mu\text{-}SPPh_2)_2(CNMe)_2]\cdot CHCl_3$ has been determined from single-crystal X-ray data collected by counter methods. The structure was solved with use of the nonstandard triclinic unit cell $P\bar{1}$ with dimensions $a = 11.268$ (4) Å, $b = 14.402$ (7) Å, $c = 11.790$ (3) Å, $\alpha = 85.55$ (3)°, $\beta = 70.09$ (2)°, and $\gamma = 68.26$ (3)°. The standard dimensions for the reduced cell were $a = 11.790$ (3) Å, $b = 14.402$ (8) Å, $c = 11.268$ (4) Å, $\alpha = 111.74$ (3)°, $\beta = 109.91$ (2)°, and $\gamma = 85.55$ (3)°. The calculated and observed densities, $Z = 2$, are 1.69 and 1.68 g cm^{-3}, respectively. Full-matrix least-squares refinements gave discrepancy factors of $R_F = 0.028$ and $R_{wF} = 0.046$ for 4856 reflections with $I_o > 3\sigma(I)$. The structure determination has shown that the palladium(I) atoms are directly bonded. The Pd–Pd distances in the two independent molecules are 2.608 (1) and 2.600 (1) Å. The other distances around Pd are as follows: Pd–S, 2.394 (1) and 2.382 (1) Å; Pd–P, 2.230 (1) and 2.239 (1) Å; Pd–C, 2.021 (4) and 2.009 (4) Å.

Introduction

Recently we reported a convenient synthesis of bis(μ-chalcogenophosphinito)bis(triorganophosphine)dimetal(I) complexes of palladium and platinum, $[M_2(\mu\text{-}EPR'_2)_2(PR_3)_2]$ (M = Pd, Pt; E = S, Se; R, R′ = alkyl, aryl), by treatment of $M(PR_3)_4$ with $R'_2P(E)H$.[3a] Besides our interest in this, to our knowledge unprecedented, reaction of $M(PR_3)_4$ with an HX compound, which results in the formation of a dimetal(I) complex and dihydrogen, these complexes have drawn our attention since they permit the study of the mutual influence of the metal–metal and bridging bonds in these systems. Further, they are among a few dipalladium(I) and diplatinum(I) complexes so far described[3-5] in which the restricted flexibility of the bridging ligands forces the coordination planes of both metal atoms into coplanarity.[6] This particular question, studied mainly by ^{31}P NMR spectroscopy for a whole series of complexes, will be discussed elsewhere.[7] This paper is concerned with ligand-exchange reactions of these complexes and attempts to achieve insertion reactions into the metal–metal bonds as well as the structures of the new complexes obtained.

Experimental Section

General Considerations. All reactions were carried out anaerobically with use of conventional Schlenk techniques. Solvents were dried, deoxygenated, and distilled just prior to use. The starting complexes, $[M_2(\mu\text{-}SPR'_2)_2(PR_3)_2]$, were prepared by the previously reported method.[3a] $P(OPh)_3$,[8] $PhP(OPh)_2$,[9] CNMe, CN-*t*-Bu,[10] and dppm[11] were prepared according to literature procedures.

NMR spectra were measured on a Bruker WP 200 NMR spectrometer operating at 200.132 MHz and 296 K (^1H), 81.026 MHz and 302 K (^{31}P), and 43.02 MHz and 302 K (^{195}Pt). Chemical shift references are the absolute frequencies of Me_4Si (^1H), external 85% H_3PO_4 (^{31}P), and 1 M Na_2PtCl_6 solution in D_2O (^{195}Pt) at the same lock (H_0) conditions. Positive shifts are to lower field. Spectral simulations were made with use of the PANIC NMR synthesis program provided by Bruker as part of the standard software for the Aspect 2000 computer. The relative signs of $^3J(P^1P^2)$, $^2J(P^1P^3)$, and $^3J(P^1P^4)$ could only be established by spectral simulation, with $^3J(P^3P^4)$ taken as positive.[12]

Ligand-Exchange Reactions (1–14). A benzene solution or suspension (40 mL) containing 1 mmol of $[M_2(\mu\text{-}SPR_2)_2(PPh_3)_2]$ and 3 mmol of $P(OPh)_3$, $PhP(OPh)_2$, or dppm or 20 mmol of CNR (R = Me, *t*-Bu) was boiled for 30 min (in the case of **14**, for 12 h) and subsequently stirred for 12 h. Solvent was removed from the resulting clear yellowish solution by vacuum evaporation until crystals began to form. Subsequent addition of *n*-hexane (for **10**, diethyl ether) gave the products, which were filtered off, washed with diethyl ether (20 mL), and recrystallized. Details are given in Table I.

X-ray Data Collection. An orange-yellow fragment of approximate size 0.17 × 0.38 × 0.42 mm was cut from a larger crystal of $[Pd_2(\mu\text{-}SPPh_2)_2(CNMe)_2]\cdot CHCl_3$ and mounted on a Syntex $P2_1$ automatic diffractometer (Mo K$\bar{\alpha}$ radiation, $\lambda = 0.71069$ Å, graphite monochromator). Fifteen intense reflections were precisely centered and yielded the nonstandard triclinic cell constants $a = 11.268$ (4) Å, $b = 14.402$ (7) Å, $c = 11.790$ (3) Å, $\alpha = 85.55$ (3)°, $\beta = 70.09$ (2)°, and $\gamma = 68.26$ (3)°, which were used for the solution and refinement of the structure. The standard reduced cell can be obtained from the transformation

$$\begin{pmatrix} 0.0 & 0.0 & 1.0 \\ 0.0 & 1.0 & 0.0 \\ -1.0 & 0.0 & 0.0 \end{pmatrix}\begin{pmatrix} x_0 \\ y_0 \\ z_0 \end{pmatrix} = \begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

where x_0, y_0, z_0 and x, y, z are the parameters for the old and new cells, respectively. The constants for the new cell are $a = 11.790$ (3) Å, $b = 14.402$ (8) Å, $c = 11.268$ (4) Å, $\alpha = 111.74$ (3)°, $\beta = 109.91$ (2)°, and $\gamma = 85.55$ (3)°.

Intensities were measured for 6440 reflections of the form h, $\pm k$, $\pm l$ in the region $2.5° \leq 2\theta \leq 50.0°$. From these, 4856 unique observed

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Table I. Preparative Details and Elemental Analyses for Compounds **1-14**

					anal. found (calcd)				
no.	dec pt, °C	% yield	color	recryst solvent	% M	% P	% C	% H	% other
1	197	92	off-white	$C_6H_6/n\text{-}C_6H_{14}$	16.5 (16.78)	9.5 (9.77)	56.32 (56.84)	3.71 (3.98)	
2	102	73	off-white	$C_6H_6/n\text{-}C_7H_{16}$		11.3 (11.52)	47.15 (49.13)	4.68 (4.69)	
3	178-180	97	off-white	$C_6H_6/n\text{-}C_6H_{14}$	*a*				
4	204-206	98	off-white	$CHCl_3$/ether	*a*				
5	230-232	38	pale yellow	$C_6H_6/n\text{-}C_6H_{14}$	*a*				
6 [6]	183-185	98	off-white	$C_6H_6/n\text{-}C_6H_{14}$			41.8 (42.10)	3.92 (4.02)	
7	301-304	91	off-white	$CHCl_3/n\text{-}C_7H_{16}$			49.90 (50.99)	3.50 (3.57)	4.30 (S) (4.54)
8	159-162	97	off-white	$CHCl_3/n\text{-}C_6H_{14}$			44.80 (43.28)	4.10 (4.13)	5.30 (S) (5.25)
9	171	92	off-white	$C_6H_6/n\text{-}C_6H_{14}$			40.80 (41.12)	3.60 (3.92)	
10	243	83	pale yellow	$CHCl_3/n\text{-}C_7H_{16}$	27.1 (28.6)	8.2 (8.33)	41.84 (45.23)	3.88 (3.53)	5.27 (N) (3.77)
11	235-237	85	pale yellow	$C_6H_6/n\text{-}C_6H_{14}$	25.80 (26.16)	7.8 (7.61)	51.40 (50.19)	4.81 (4.71)	3.26 (N) (3.44)
12	194-198	85	pale yellow	$C_6H_6/n\text{-}C_6H_{14}$		8.2 (8.97)	21.92 (20.17)	4.22 (3.67)	5.99 (N) (3.92)
13	104-106	75	off-white	$C_6H_6/n\text{-}C_6H_{14}$	38.6 (39.37)	6.1 (6.25)	41.45 (41.21)	4.07 (3.87)	2.76 (N), 5.71 (S) (2.83), (6.47)
14[b]	243	94	yellow	$C_6H_6/n\text{-}C_6H_{14}$	30.1 (30.36)	14.2 (14.46)			

[a] Only identified by spectroscopic means. [b] Molecular weight: calcd ($C_{74}H_{64}P_6Pt_2S_2$), 1285.06; found, 1279 (cryoscopically in benzene).

($I \geq 3\sigma(I)$) reflections were obtained by averaging. Gaussian integration absorption corrections[13] were applied (μ = 15.44 cm^{-1}), yielding transmission coefficient that varied from 1.297 to 1.593. Other details of data collection are given in Table II.

Solution and Refinement of the Structure. The centric space group[14] $P\bar{1}$ was assumed and gave satisfactory refinement throughout. This choice required the location of two half-molecules, which generated the full unit cell through the center of inversion. The positions of the two independent Pd atoms were obtained from calculations on a three-dimensional Patterson map. All other non-hydrogen atoms were located from a series of Fourier maps and their positions and temperature factors refined by least-squares techniques.[3b] Hydrogen atoms were placed by a combination of observed and calculated positions and given arbitrary isotropic temperature factors of 4.0 Å.[3a] It was difficult to locate reasonable positions for the methyl hydrogen atoms in the CNMe molecules, so these were not included in the final model. All parameters associated with hydrogen were held fixed throughout refinement. Full-matrix least squares[15] using our usual weighting scheme[16] yielded residual indices[17] of R_F = 0.028 and R_{wF} = 0.046. At this point two atoms, C63 and C71, were exhibiting least-squares shifts on the order of 1σ in their temperature parameters. After 10 additional cycles of least squares, these shifts remained on the order of 1σ and refinement was halted. The maximum shift for the parameters associated with all other atoms was less than 0.1σ. In the final least squares, the number of variables was 361, the number of observed data was 4856, and the error in an observation unit weight was 1.52. The largest peak on a final difference map represents less than one electron and is in the vicinity of C63. The error of fit changes only slightly over intervals of (sin θ)/λ, but the trend indicates that p in the calculation of I was probably underrated. p had been assigned the value 0.05.

Table II. Experimental Data from the X-ray Diffraction Study on [$Pd_2(\mu\text{-}SPPh_2)_2(CNMe)_2$]·$CHCl_3$

formula: $Pd_2C_{14}H_{16}N_2P_2S_2\cdot CHCl_3$
mol wt: 551.01; 119.37
cryst dimens: 0.38 × 0.38 × 0.15 mm^3
cryst syst: triclinic
space group: $P\bar{1}$
cell dimens:[a] a = 11.268 (4) Å, b = 14.402 (7) Å, c = 11.790 (3) Å, α = 85.55 (3)°, β = 70.09 (2)°, γ = 68.26 (3)°
reduced cell dimens: a = 11.790 (3) Å, b = 14.402 (8) Å, c = 11.268 (4) Å, α = 111.74 (3)°, β = 109.91 (2)°, γ = 85.55 (3)°
V = 1668 (1) Å^3
Z = 2
D_{obsd} = 1.68 g/cm^3 (neutral buoyancy in $CHCl_3/CHBr_3$)
D_{calcd} = 1.69 g/cm^3
radiation: Mo K$\bar{\alpha}$ (λ = 0.710 69 Å)
monochromator: graphite crystal
rflctn measd: $h, \pm k, \pm l$
2θ range: 2.5° $\leqslant 2\theta \leqslant$ 50.0°
scan speed: 2.0-4.0°/min
scan width: 0.9° below Kα_1 to 0.9° above Kα_2 in 2θ
bkgd. measmt: stationary cryst-stationary counter at beginning and end of 2θ, each for $^1/_4$ the time taken for the 2θ scan
std rflctns: 3 measd every 97 rflctns; max dev in intens for the stds random and less than 3%, therefore, no decay cor applied
unique data: 6440 (total measd)
unique data with $F^2 \geqslant 3\sigma(I)$: 4856
abs coeff: μ = 13.10 cm^{-1}
$F(000)$: 840 e
R_F: 0.028
R_{wF}: 0.046

[a] Lattice parameters were obtained with use of an autoindexing program and a least-squares fit to the setting at the unresolved Mo K$\bar{\alpha}$ components of 15 reflections.

Neutral-atom scattering factors[18] were used and those for Pd, Cl, S, and P corrected[19] for anomalous dispersion. Final positional parameters are presented in Table III. Selected interatomic distances and angles are listed in Table IV. The errors were estimated by the variance-covariance method. Lattice errors were not included. Full listings of interatomic distances (Table S-I) and angles (Table S-II), anisotropic thermal parameters (Table S-III), least-squares planes (Table S-IV), hydrogen atom positional parameters (Table S-V), and observed and calculated structure amplitudes (Table S-VI) are available.[20]

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(13) Computing programs were local modifications of D. Templeton and L. Templeton's ABSORB, Zalkin's FORDAP, Johnson's ORTEP, and Busing, Martin, and Levy's ORFLS and ORFEE.
(14) "International Tables for X-ray Crystallography", 3rd ed.; Kynoch Press: Birmingham, England, 1969; Vol. 1.
(15) The function minimized was $w(|F_o| - |F_c|)^2$.
(16) $w = 1/\sigma^2(F_o)^2$.
(17) $R_F = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_{wF} = [\Sigma_w(|F_o| - |F_c|)^2]^{1/2}/[\Sigma_w F_o^2]^{1/2}$.
(18) Cromer, D. J.; Mann, J. B. *Acta Crystallogr., Sect. A* **1968**, *A24*, 321.
(19) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. 4, p 149.
(20) See the paragraph at the end of the paper regarding supplementary material.

Table III. Atomic Coordinates for the Non-Hydrogen Atoms in $[Pd_2(\mu\text{-}SPPh_2)_2(CNMe)_2]\cdot CHCl_3$

atom	x	y	z
Pd1	0.03381 (3)	−0.06672 (2)	−0.08544 (3)
Pd2	0.54350 (3)	0.50018 (2)	0.38277 (2)
S1	0.1076 (1)	−0.1997 (1)	0.0391 (1)
P1	−0.0571 (1)	0.0825 (1)	−0.1535 (1)
S2	0.6576 (1)	0.6077 (1)	0.3928 (1)
P2	0.4136 (1)	0.4075 (1)	0.4267 (1)
Cl1	−0.1990 (2)	−0.3255 (1)	0.1111 (1)
Cl2	0.0260 (2)	−0.3898 (1)	−0.1127 (2)
Cl3	−0.2308 (2)	−0.2483 (1)	−0.1140 (2)
C11	0.2113 (4)	−0.0958 (3)	0.1818 (4)
C12	0.2675 (5)	−0.0217 (4)	0.1502 (5)
C13	0.3872 (6)	−0.0327 (4)	0.1662 (6)
C14	0.4519 (6)	−0.1179 (5)	0.2165 (6)
C15	0.3992 (6)	−0.1916 (5)	0.2485 (6)
C16	0.2784 (6)	−0.1804 (4)	0.2318 (5)
C21	−0.0537 (4)	−0.1022 (3)	0.3006 (4)
C22	−0.1374 (5)	−0.1550 (3)	0.3082 (4)
C23	−0.2271 (5)	−0.1663 (4)	0.4171 (5)
C24	−0.2346 (6)	−0.1237 (4)	0.5193 (5)
C25	−0.1555 (6)	−0.0688 (5)	0.5139 (4)
C26	−0.0644 (6)	−0.0588 (4)	0.4052 (4)
C31	0.2667 (4)	0.4647 (3)	0.3784 (3)
C32	0.2321 (4)	0.5636 (3)	0.3468 (4)
C33	0.1150 (5)	0.6107 (4)	0.3176 (5)
C34	0.0338 (5)	0.5604 (4)	0.3195 (4)
C35	0.0664 (5)	0.4623 (4)	0.3515 (5)
C36	0.1826 (5)	0.4136 (3)	0.3797 (4)
C41	0.4941 (4)	0.2822 (3)	0.3499 (4)
C42	0.5434 (5)	0.1980 (4)	0.4102 (5)
C43	0.6053 (6)	0.1035 (4)	0.3488 (7)
C44	0.6202 (5)	0.0957 (4)	0.2283 (7)
C45	0.5722 (6)	0.1789 (5)	0.1683 (5)
C46	0.5101 (5)	0.2730 (4)	0.2289 (5)
C51	0.0846 (5)	−0.1559 (3)	−0.2318 (4)
N52	0.1183 (4)	−0.2054 (3)	−0.3159 (4)
C53	0.1656 (7)	−0.2717 (5)	−0.4220 (5)
C61	0.6032 (5)	0.4932 (4)	0.2015 (4)
N62	0.6417 (5)	0.4888 (3)	0.0979 (3)
C63	0.7030 (8)	0.4755 (6)	−0.0314 (5)
C71	−0.1222 (6)	−0.2908 (4)	−0.0312 (5)

Table IV. Selected Interatomic Distances (Å) and Angles (deg) for $[Pd_2(\mu\text{-}SPPh_2)_2(CNMe)_2]\cdot CHCl_3$

	Molecule 1		
Pd1-Pd1	2.608 (1)	P1-C11	1.818 (4)
Pd1-P1	2.230 (1)	P1-C21	1.833 (4)
Pd1-S1	2.394 (2)	C51-N52	1.135 (6)
Pd1-C51	2.021 (4)	N52-C53	1.454 (6)
P1-S1	2.028 (2)		
S1-Pd1-P1	164.0 (1)	Pd1-P1-S1	114.0 (1)
Pd1-Pd1-C51	172.9 (1)	Pd1-C51-N52	177.1 (4)
Pd1-S1-P1	81.6 (1)		
	Molecule 2		
Pd2-Pd2	2.600 (1)	P2-C31	1.817 (4)
Pd2-P2	2.239 (1)	P2-C41	1.838 (4)
Pd2-S2	2.382 (1)	C61-N62	1.146 (6)
Pd2-C61	2.009 (4)	N62-C63	1.439 (7)
P2-S2	2.029 (2)		
S2-Pd2-P2	164.7 (1)	Pd2-P2-S2	111.3 (1)
Pd2-Pd2-C61	175.5 (1)	Pd2-C61-N62	177.6 (5)
Pd2-S2-P2	83.7 (1)		

Description of the Structure of $[Pd_2(\mu\text{-}SPPh_2)_2(CNMe)_2]\cdot CHCl_3$

The unit cell consists of two molecules of the cyclic dimer $[Pd_2(\mu\text{-}SPPh_2)_2(CNMe)_2]$, which is shown in Figure 1 separated by chloroform molecules. The packing arrangement is shown in Figure 2 and indicates that there are no significant intermolecular interactions. Each of the two independent dimeric units contains a crystallographic center of inversion. The Pd–Pd distances within the dimers are 2.608 (1) and 2.600 (1) Å, respectively, and are relatively short compared to those of other systems containing Pd–Pd bonds (the range of observed Pd–Pd distances is 2.57–2.75 Å), suggesting relatively strong interactions. The other distances around the Pd atoms are within the normal range observed for Pd–S, Pd–P, and Pd–C bonds. The S–P (2.028 Å) bond is shorter than that observed in related phosphine sulfides (2.006 Å)[21] and is slightly shorter than that observed in the platinum derivative $[Pt_2(\mu\text{-}SPEt_2)_2(P(OPh)_3)_2]$,[6] suggesting increased bond order.

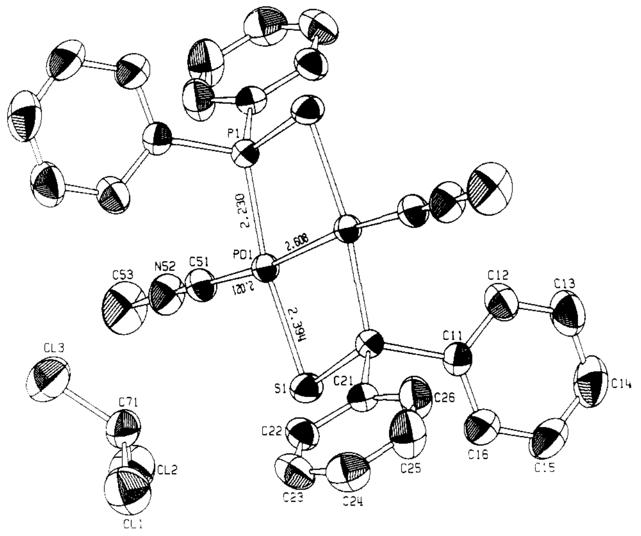

Figure 1. ORTEP drawing of a molecule of $[Pd_2(\mu\text{-}SPPh_2)_2(CNMe)_2]\cdot CHCl_3$ with the atoms labeled.

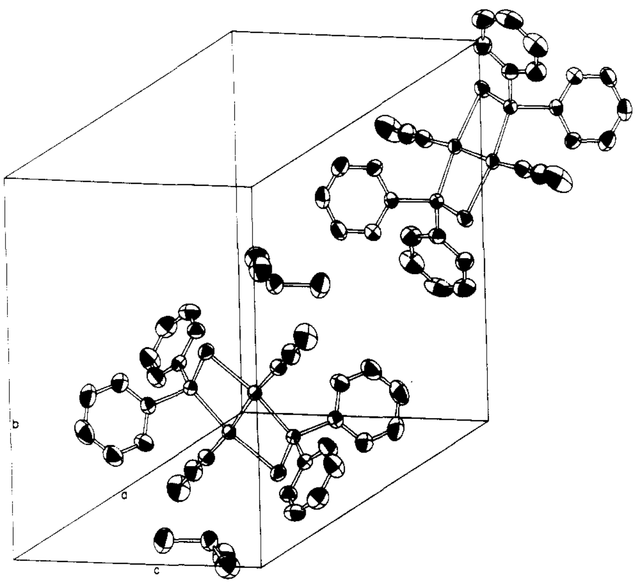

Figure 2. Three-dimensional view of the packing in $[Pd_2(\mu\text{-}SPPh_2)_2(CNMe)_2]\cdot CHCl_3$.

The entire central molecular framework, including the Pd atoms and all of those atoms directly bound to them, is coplanar, with the maximum deviation from planarity being 0.03 Å (see Table IV), again similar to the case for the Pt derivative.

Results and Discussion

Synthetic Studies. Treatment of $[M_2(\mu\text{-}SPR_2)_2(PPh_3)_2]$ with excess $P(OPh)_3$ or $PhP(OPh)_2$ (mole ratio 1:3) or CNR′ (R′

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[21] The average P–S single-bond distance in 2-methyl-2-thioxo-1,3-dithia-2-phosphorinane ($\overline{SCH_2CH_2CH_2SP}(S)CH_3$) is 2.066 Å and in 2-chloro-2-thioxo-1,3-dithia-2-phosphorinane ($\overline{SCH_2CH_2CH_2SP}(S)Cl$) is 2.051 Å: Grand, P. A.; Martin, J.; Robert, J. B. *Acta Crystallogr., Sect. B* **1976**, *B32*, 1244.

= Me, *t*-Bu; mole ratio 1:20) in benzene readily yields the ligand-exchange products **1**–**13** according to eq 1. Surprisingly, $[M_2(\mu\text{-}SP(OEt)_2)_2(PPh_3)_2]$ did not give exchange reactions with $P(OPh)_3$ and CN-*t*-Bu whereas it did react with $PhP(OPh)_2$ to give **9**.

$$[M_2(\mu\text{-}SPR_2)_2(PPh_3)_2] + 2L \xrightarrow{-2PPh_3} [M_2(\mu\text{-}SPR_2)_2L_2] \quad (1)$$

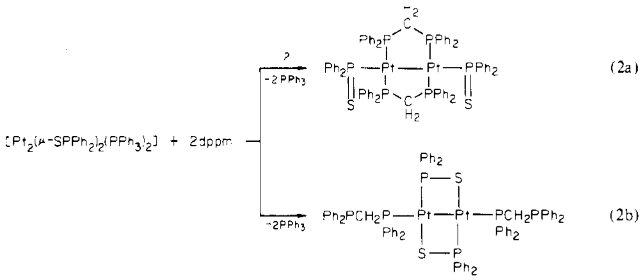
	1	2	3	4	5
M	Pd	Pd	Pd	Pt	Pt
R	Ph	Et	Et	Ph	Cy
L	$P(OPh)_3$	$P(OPh)_3$	$PPh(OPh)_2$	$P(OPh)_3$	$P(OPh)_3$

	6	7	8	9
M	Pt	Pt	Pt	Pt
R	Et	Ph	Et	OEt
L	$P(OPh)_3$	$PPh(OPh)_2$	$PPh(OPh)_2$	$PPh(OEt)_2$

	10	11	12	13
M	Pd	Pd	Pt	Pt
R	Ph	Ph	Et	Ph
L	CNMe	CN-*t*-Bu	CNMe	CN-*t*-Bu

Ph_2POPh, $P(NMe_2)_3$, $As(OEt)_3$, $EtO(O)C{-}C{\equiv}C{-}C(O)OEt$, and maleic anhydride did not react at all with $[M_2(\mu\text{-}SPR_2)_2(PPh_3)_2]$ even after prolonged boiling in benzene. Ph_2PCl, $PhPCl_2$, PCl_3, and $AsCl_3$ reacted vigorously at ambient temperatures but did not yield single, identifiable products, likely because of competing chlorination reactions. **6** and $[Pt_2(\mu\text{-}SPMe_2)_2(P(OPh)_3)_2]$ previously had been obtained by the same reaction type by Treichel et al.[6] and $[Pt_2(\mu\text{-}SPMe_2)_2(P(OMe)_3)_2]$ had been obtained by Boag et al.[12] In particular, Balch's[22] and Brown's[23] groups have shown the marked tendency of the (diphenylphosphino)methane (dppm) ligand to doubly bridge two palladium or platinum atoms, forming the $[M_2(\mu\text{-dppm})_2]$(*M*–*M*) unit.

Therefore, we were interested in treating $[Pt_2(\mu\text{-}SPPh_2)_2(PPh_3)_2]$ with dppm to explore whether this ligand would be capable of forcing the μ-$SPPh_2$ ligand into a terminal P- (or S-) bonded thiophosphinito ligand according to eq 2a. After several hours in boiling benzene (mole ratio 1:3) the reaction yielded a yellow crystalline complex, which was assigned the structure **14** in solution (eq 2b) on the basis of the NMR spectra. As expected, bis(diphenylarsino)methane does not react with $[Pt_2(\mu\text{-}SPPh_2)_2(PPh_3)_2]$.



Attempts to react the uncoordinated PPh_2 groups of the dppm ligands of **14** with MeI led to the decomposition of the $[Pt_2(\mu\text{-}SPPh_2)_2]$ unit, but it seems that **14** reacts with $(CO)_5Cr{\cdot}THF$ with coordination of two $Cr(CO)_5$ groups to these phosphorus atoms.

CO does not react at all with $[M_2(\mu\text{-}SPR'_2)_2(PR_3)_2]$ under normal pressure. The starting complexes could be completely recovered. $[Pt_2(\mu\text{-}SPEt_2)_2(PPh_3)_2]$ in benzene reacts very slowly with S_8, but an unidentifiable mixture of products is formed. Complexes $[M_2(\mu\text{-}SPR'_2)_2(PR_3)_2]$ in chloroform or benzene spontaneously react with sulfur dioxide to yield deep red solutions. Crystals of the same color could be obtained from highly concentrated SO_2-saturated benzene solutions after the solution stood for several days in a refrigerator. However, both solutions and crystals readily lose sulfur dioxide under vacuum or on standing to re-form the parent complexes, thus preventing elemental analysis.

In summary, $[M_2(\mu\text{-}SPR'_2)_2(PR_3)_2]$ complexes appear to undergo facile ligand exchange, but there is some evidence that these molecules, unlike complexes with the $[M_2(\mu\text{-dppm})_2]$(*M*–*M*) unit,[22,23] do not show the tendency to insert small molecules into its metal–metal bond. Clearly, the coordination unsaturation of the metal centers surrounded by 16 electrons makes the metals accessible to incoming nucleophiles, thus supporting reactivity and allowing ligand-exchange reactions. On the other hand, the restricted flexibility of these molecules, due to the strong μ-SPR'_2 ligands, seems to prevent these molecules from achieving the structural rearrangement required for insertion reactions. The ability of the μ-$SPPh_2$ ligand to double-bridge two Pt(II) centers has recently been shown by the synthesis of $[Pt_2(\mu\text{-}SPPh_2)_2(S_2CNR_2)_2]$.[24] Further attempts will be made to oxidize $[M_2(\mu\text{-}SPR'_2)_2(PR_3)_2]$ to the M(II) complexes $[M_2(\mu\text{-}SPR'_2)_2(PR_3)_2L_2]$ (L = uninegative, monodentate ligand).

Spectroscopic Measurements. The $^{31}P\{^1H\}$ NMR and fundamental IR data of **1**–**6** and **8**–**14** are collected in Table V. The spectrum of **7** could not be obtained due to lack of its solubility in $CDCl_3$ or C_6D_6. In contrast to the simple AX spectra of the dipalladium complexes **1**–**3**, those of the diplatinum complexes **4**–**9** are complicated by the various couplings within the three isotopomers, containing no, one, and two ^{195}Pt nuclei ($I = {}^1/_2$), respectively (Figure SI[20] gives the $^{31}P\{^1H\}$ NMR spectrum of **6**, which shows the various ^{195}Pt couplings). Their analysis was carried out as described previously.[3a]

The spectra of **12** and **13** consist of a single line for that isotopomer without ^{195}Pt superimposed by the ABX system of the $[^{195}PtPt(\mu\text{-}SPR_2)_2L_2]$ isotopomer (44.8%) and the AA′XX′ system of the $[^{195}Pt_2(\mu\text{-}SPR_2)L_2]$ isotopomer (11.4%) with the labels A, B = ^{31}P, and X = ^{195}Pt. The analysis of these second-order spectra is straightforward[25] and yields $^1J(^{195}Pt^{31}P)$, $^2J(^{195}Pt^{31}P)$, $^3J(^{31}P^{31}P)$, and $^1J(^{195}Pt^{195}Pt)$. A large excess of CNR does not affect the spectroscopic parameters, whereas they are markedly dependent on temperature.[7] The ^1H NMR spectra in 1:1 $CDCl_3/CD_2Cl_2$) of **10**, **12**, and **13** exhibit a single line for the protons of the CNR ligands down to −90 °C (**10**, 3.07 ppm; **12**, 3.0(Me) and 1.76(Et) ppm, with $^3J(PCH) = 17.7$ Hz, $^3J(CH_2CH_3) = 14.6$ Hz, and $^4J(PtCNCH) = 13.4$ Hz; **13**, 1.18 ppm). The intensity ratio of the Et protons of the bridging ligands and the Me protons of the terminal CNMe ligands is in accord with the presence of only two CNR ligands. The $^4J(PtCNCH)$ coupling in the spectrum of **12** excludes rapid ligand exchange. Thus, the spectra prove, in accord with the molecular structure of **10**, that no insertion of CNR into the metal–metal bond had occurred during the reaction of $[M_2(\mu\text{-}SPR_2)_2(PPh_3)_2]$ with excess CNR despite the unsatisfactory elemental analyses of **10** and **12**, which would, in fact, agree with such a complex. In contrast, **11** and **13** gave correct analyses.

The ^{31}P spectrum of **14** exhibits three chemically inequivalent ^{31}P nuclei, two of them showing the typical pattern of the $[Pt_2(\mu\text{-}SPR'_2)(PR_3)_2]$ complexes except one additional $^{31}P^{31}P$ coupling of 30.2 Hz for the terminal-bonded phosphorous nuclei P^3 and P^4. This coupling also appears in the signal of the noncoordinated phosphorous groups of the dppm

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Table V. NMR and IR Parameters for Compounds 1-14[a]

		$^{31}P\{^1H\}$ NMR											IR (KBr)	
no.	solvent	$\delta(P^1,P^2)$	$\delta(P^3,P^4)$	J(PtPt)	$^1J(P^1Pt^X)$	$^2J(P^2Pt^X)$	$^3J(P^1P^2)$	$^1J(P^3Pt^X)$	$^2J(P^4Pt^X)$	$^3J(P^3P^4)$	$^2J(P^1P^3)$	$^3J(P^1P^4)$	ν(PS)	ν(CN)
1	C_6D_6	24.2	108.2	...	...	...	...	...	...	...	*b*	...	580	...
2	C_6D_6	37.2	112.3	...	...	...	...	...	...	...	7.5	...	550	...
3	C_6D_6	41.8	139.1	...	...	...	...	...	...	...	7.5	...	552	...
4	$CDCl_3$	1.56	103.23	5.78	+3410.1	−155.3	−8.8	+4607.0	+799.7	+584.6	−14	−11	580	...
5	CD_2Cl_2	32.0	109.58	494.6	+3271.6	−62.2	−5.0	+4318.2	+998.3	+647.7	−16.1	−2.8	567	...
6	$CDCl_3$	17.4	108.6	464.7	+3266.9	−53.0	6.8	+4420.2	+915.4	+621.6	15.6	7.8	540	...
	$CDCl_3/SO_2$	17.2	108.5	456.9	+3255.2	+51.4	−7.4	+4408.8	+909.5	+620.0	−15.9	−7.15		
Δ^c		−0.2	−0.1	−7.8	−11.7	+1.6	...	−11.4	−5.9	−1.6	...	...		
	SO_2 (258 K)	21.0	106.5	*b*	ca. +3200	*b*	*b*	+4362.1	+836.5	+592.6	*b*	*b*		
Δ^c		+3.6	−2.1	...	...	...	...	−58.1	−79.9	−29.0	...	...		
	SO_2 (248 K)	21.5	106.2	*b*	ca. +3194	*b*	*b*	+4328.2	+820.8	+589.8	*b*	*b*		
Δ^c		+4.1	−2.4	...	...	...	...	−92.0	−94.5	−31.8	...	...		
7	*c*	...	...	...	...	...	...	...	...	...	...	...	567	...
8	C_6D_6	20.5	130.6	365.5	+3356.0	−74.7	5.9	+3778.0	+672.7	+435.1	−13.9	−4.4	560	...
9	C_6D_6	101.0	124.4	95.2	+4796.0	−249.8	11.0	+3870.9	+647.5	+355.6	14.2	9.1	620	...
10	$CDCl_3/CD_2Cl_2$	26.3	...	...	...	...	...	...	...	...	...	...	595	2200
11	$CDCl_3/CD_2Cl_2$	26.7	...	...	...	...	...	...	...	...	...	...	595	2170
12	$CDCl_3/CD_2Cl_2$	7.5	...	1022	+3456	−60	9.8	...	...	...	...	...	550	2189, 2218
13	$CDCl_3/CD_2Cl_2$	−2.7	...	1163	+3590	−151	8.5	...	...	...	...	...	585	2165
14[d]	$CDCl_3$	10.72	8.23	430	+3683.1	−216.1	11.5	+2739.8	+445.2	+215.2	7.0	5.0	578	...

[a] Atom labeling is given by

For **10-13**, CNR instead of P^3, P^4. [b] Not observed. [c] See text. [d] Noncoordinated ^{31}P nuclei of dppm P^5 and P^6: $\delta = -26.13$ ppm, $^2(P^3P^5) = {}^2J(P^4P^6) = 30.2$ Hz.

ligands. In the ^1H spectrum the signal due to the CH_2 protons of dppm exhibits a broad unresolved peak at 2.9 ppm. This lends support to the structure proposed because the alternative structure containing the $[Pt_2(\mu\text{-dppm})_2]$ unit should give five peaks of relative intensity 1:8:17:8:1 with peak separations equal to $^1/_2[^3J(^{195}Pt^1H)]$.[26] It should be mentioned, however, that the solid-state structure of **14**, which has not yet been elucidated, due to lack of suitable single crystals, might be different from that in solution and moreover might depend on the solvent from which **14** is precipitated.

In the $^{195}Pt\{^1H\}$ NMR spectra of **4** (C_6D_6) and **5** (CD_2Cl_2) only the 16 lines of the most abundant ABMNX system (with the labels A, B, M, N = ^{31}P, and X = ^{195}Pt) centered at −5135 and −5216 ppm, respectively, could be observed. These values agree well with the −5178-ppm ($CDCl_3$) value for $[Pt_2(\mu\text{-}SPMe_2)_2(P(OMe)_3)_2]$ given by Boag et al.[12] The medium or strong frequencies in the IR spectra indicate the lower PS bond order of the μ-SPR_2 ligands compared to that of the parent secondary phosphine sulfides. According to the PS bond distances of 2.046 and 2.028 Å found for $[Pt_2(\mu\text{-}SPEt_2)_2(P(OPh)_3)_2]$[6] and **10**, respectively, as well as ESCA measurements,[27] the bond order should be close to 1.5. The IR spectra of **10-13** display strong ν(CN) frequencies in the 2150-2200-cm^{-1} range as anticipated for terminal-bonded CNR ligands. There are no bands in the 1600-1700-cm^{-1} range, where these bands are to be expected in the case of bridging CNR groups.

The IR (Nujol) spectra of the SO_2 adducts are essentially identical with those of the parent complexes. Significant features that differentiate the IR spectrum of the SO_2 adduct of $[Pt_2(\mu\text{-}SPPh_2)_2(PMePh_2)_2]$ from that of the parent complex are two additional bands at 1085 and 1250 cm^{-1}, which are assigned to the symmetric and antisymmetric SO stretching vibrations, respectively.

Table V also contains the NMR data of **6** in SO_2-saturated $CDCl_3$ solution as well as in liquid SO_2 at 258 and 248 K and compares these data with those of the parent complex (Δ). Figure SI[20] shows the $^{31}P\{^1H\}$ spectrum of **6** in liquid SO_2 at 245 K. Whereas the spectrum of the SO_2-saturated $CDCl_3$ solution does not differ significantly from that of **6**, the spectra in liquid SO_2 show a significant broadening of the signals due to the bridging ligands, thus preventing a detailed analysis to be made of this part of the spectrum, although they maintain the typical pattern of the collinear P-Pt-Pt-P unit. There are significant changes in both the chemical shifts and the coupling constants for the phosphorus atoms. Part of the observed changes may be attributed to solvent effects, but larger changes associated with bridging P atoms and the broadening of these resonance lines suggest that there are additional processes occurring. We conclude from this spectroscopic behavior that (a) SO_2 does not insert into the metal-metal bond and (b) an equilibrium exists, clearly dependent upon both the temperature and the sulfur dioxide concentration, between the parent complex and a sulfur dioxide containing complex in which the SO_2 is reversibly coordinated involving the bridging ligands. To date, no reasonable suggestion can be made about the coordination mode of SO_2 in this complex.

Acknowledgment. We thank Mr. A. Haman for preparing the compounds **3**, **7**, **8**, and **9**. NSF grants CHE-79-13182 and CHE-80-16862 provided partial support for this work.

Registry No. **1**, 83666-18-6; **2**, 83681-32-7; **3**, 83666-19-7; **4**, 83681-33-8; **5**, 83666-20-0; **6**, 54020-39-2; **7**, 83666-21-1; **8**, 83666-22-2; **9**, 83666-23-3; **10**, 83666-25-5; **11**, 83666-26-6; **12**, 83666-27-7; **13**, 83666-28-8; **14**, 83666-29-9; $[Pd_2(\mu\text{-}SPEt_2)_2(PPh_3)_2]$,

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83681-34-9; $[Pt_2(\mu\text{-}SPPh_2)_2(PPh_3)_2]$, 67275-91-6; $[Pt_2(\mu\text{-}SPEt_2)_2(PPh_3)_2]$, 54020-36-9; $[Pt_2(\mu\text{-}SPCy_2)_2(PPh_3)_2]$, 74353-71-2; $[Pd_2(\mu\text{-}SPPh_2)_2(PPh_3)_2]$, 67275-92-7; $[Pt_2(\mu\text{-}SPOEt_2)_2(PPh_3)_2]$, 83666-30-2.

Supplementary Material Available: The $^{31}P\{^1H\}$ NMR spectrum of $[Pt_2(\mu\text{-}SPEt_2)(P(OPh)_3)_2]$ and listings of all interatomic distances and angles, hydrogen positional parameters, anisotropic thermal parameters for non-hydrogen atoms, least-squares planes, and observed and calculated structure amplitudes (×10) (30 pages). Ordering information is given on any current masthead page.

Contribution from Laboratoire de Chimie des Métaux de Transition, Equipe de Recherche associée au CNRS No. 608, Université Pierre et Marie Curie, 75230 Paris Cedex 05, France

Substitution Derivatives of the Mixed-Valence $[W_4O_8Cl_8(H_2O)_4]^{2-}$ Ion. Crystal and Molecular Structure of $Cs_5NH_4[W_4O_8(NCS)_{12}]\cdot 6H_2O$

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Mixed-valence complexes containing the $W_4O_8^{6+}$ core have been prepared from $[W_4O_8Cl_8(H_2O)_4]^{2-}$. These include $[W_4O_8Cl_6(DMF)_6]$, $[W_4O_8(NCS)_{12}]^{6-}$, and $[W_4O_8(NCS)_4(C_2O_4)_4]^{6-}$. The cesium ammonium salt $Cs_5NH_4[W_4O_8(NCS)_{12}]\cdot 6H_2O$ crystallizes in the orthorhombic space group $Pna2_1$ with $a = 17.938$ (3) Å, $b = 13.395$ (6) Å, $c = 21.448$ (9) Å, and $Z = 4$. The structure has been solved from 2354 observed reflections. Full-matrix least-squares refinements led to the final agreement factors $R = 0.073$ and $R_w = 0.080$. The $[W_4O_8(NCS)_{12}]^{6-}$ anion exhibits a planar W_4O_4 ring. The terminal (unshared) oxygen atoms are found in a "chair" arrangement, which differs from the case of $[W_4O_8Cl_8(H_2O)_4]^{2-}$. This could be explained by an interaction with Cs^+ cations in the solid state. No crystallographic evidence for valence trapping has been observed.

Introduction

In the framework of a general study of mixed-valence compounds on an experimental[1] as well as a theoretical basis,[2] we have tried to prepare some new compounds containing a tetranuclear arrangement. In a previous paper, we described the structure and properties of the mixed-valence $[W_4O_8Cl_8(H_2O)_4]^{2-}$ ion.[3] This species is obtained by an equilibrated reaction between $W^{VI}O_2Cl_4^{2-}$ and $W^VOCl_5^{2-}$ in concentrated hydrochloric acid. Its crystal structure shows a nearly planar square of four tungsten atoms linked by linear oxygen bridges. In addition, each tungsten atom is linked to a terminal unshared oxygen atom so that the actual mixed-valence moiety is $W_4O_8^{6+}$. This square arrangement can be considered as a fragment of the perovskite structure of tungsten bronzes. The main interest of this compound resides in its electronic structure: owing to the presence of two tungsten(VI) and two tungsten(V) ions, it can exhibit both mixed-valence and exchange-interaction properties. This is the subject of a detailed treatment that will be published elsewhere.[4]

In order to develop the chemistry of this unique compound, we have prepared several substitution derivatives. Although the $[W_4O_8Cl_8(H_2O)_4]^{2-}$ ion does not present great thermodynamic stability since it equilibrates in solution with the monomeric W^V and W^{VI} complexes, it can be used as a starting material to prepare other compounds containing the mixed-valence $W_4O_8^{6+}$ core. We have thus prepared the species $[W_4O_8Cl_6(DMF)_6]$, $[W_4O_8(NCS)_{12}]^{6-}$, and $[W_4O_8(NCS)_4(C_2O_4)_4]^{6-}$ and solved the structure of the thiocyanate complex. This complex was the only one that gave crystals suitable for an X-ray study. The structure showed an unexpected stereochemical change of the $W_4O_8^{6+}$ geometry, due to a different disposition of unshared oxygen atoms.

Experimental Section

Synthesis from $[W_4O_8Cl_8(H_2O)_4]^{2-}$. All experiments were performed under a nitrogen or argon atmosphere.

$[W_4O_8Cl_6(DMF)_6]\cdot 2DMF$. A 1.41-g sample of $(HNMe_3)_2[W_4O_8Cl_8(H_2O)_4]\cdot 2H_2O$[3] (1.02 mmol) was dissolved in 100 mL of *N,N*-dimethylformamide. The resulting deep blue solution was filtered off to eliminate a small residue and then precipitated by 750 mL of ethyl acetate. The precipitate was filtered off, dried under vacuum for 2 days, and finally ground. Anal. Calcd: W, 44.28; Cl, 12.81; N, 6.75; C, 17.36; H, 3.40. Found: W, 44.66; Cl, 13.31; N, 6.43; C, 15.82; H, 3.53.

$Cs_5NH_4[W_4O_8(NCS)_{12}]\cdot 6H_2O$. To 500 mL of an aqueous solution of NH_4SCN (5 mol dm^{-3}) and HCl (0.05 mol dm^{-3}) was added 4.16 g of $(HNMe_3)_2[W_4O_8Cl_8(H_2O)_4]\cdot 2H_2O$ (3 mmol). The solution was filtered to remove a trace of undissolved chloride complex, and 20 g of cesium chloride was slowly added under stirring. Very small crystals appeared after 2 days at 0 °C and were washed with absolute ethanol and ether. Crystals for X-ray work were obtained by a modified procedure, using 50 mL of a solution of NH_4SCN (3 mol dm^{-3}) and HCl (0.1 mol dm^{-3}), 0.412 g of the chloride complex, and 2 g of CsCl. The solution was heated to 60 °C until the precipitate redissolved and then slowly cooled down first to 35 °C and then from 35 to 20 °C at a rate of 3 °C/day. Beautiful blue crystals with an orange metallic luster were obtained after several days. Anal. Calcd: W, 31.28; Cs, 28.26; S, 16.36; C, 6.13; N, 7.75; H, 0.69. Found: W, 32.44; Cs, 29.09; S, 16.68; C, 6.62; N, 7.83; H, 0.72. The presence of NH_4^+ was confirmed by IR spectroscopy (bands at 3120 and 1400 cm^{-1}). The number of crystallization water molecules was determined by NMR[5] as follows. The thiocyanate complex was dissolved in $(C^2H_3)_2SO$ to a concentration of 5.2×10^{-2} mol dm^{-3} and the spectrum recorded. A triplet with $J = 50$ Hz was observed at 6.95 ppm (with respect to hexamethyldisiloxane), corresponding to the NH_4^+ protons interacting with the ^{14}N nucleus, while the signal corresponding to crystallization water molecules was observed at 3.20 ppm. After taking into account the residual water of the solvent, we used this peak to determine the number of water molecules by comparison with a reference peak provided by a known amount of $CHCl_3$. This procedure yielded six molecules of crystallization water per formula unit.

$(C_9H_8N)_5(NMe_4)[W_4O_8(NCS)_4(C_2O_4)_4]\cdot 3H_2O$. The preceding preparation was repeated, but the precipitation of $[W_4O_8(NCS)_{12}]^{6-}$ was carried out by NMe_4^+ instead of Cs^+. A 600-mg sample of the tetramethylammonium salt was dissolved in 50 mL of $H_2C_2O_4$ (1 mol dm^{-3}), and the solution was precipitated by 400 mg of quinoline

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