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BIFUNCTIONAL AMINOPHOSPHANES $(Et_2N)_2P(CH_2)_nP(NEt_2)_2$ AND $(Et_2N)_2PP(NEt_2)_2$ AS LIGANDS IN METAL(0) CARBONYL COMPLEXES OF Cr, Mo AND W

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Summary

Depending on the value of n, bifunctional aminophosphanes $(Et_2N)_2P(CH_2)_n$-$P(NEt_2)_2$ (L—L) have been shown to form either mononuclear complexes $(CO)_4M$ *cis*-(L—L) (M = Cr, n = 1—4; M = Mo, W, n = 4) or binuclear compounds $[(CO)_4M(L—L)]_2$ (M = Cr, n = 5—10) with ligand bridges in *trans*-positions. By suitable choice of reaction conditions, $(CO)_5M(L—L)M(CO)_5$ (M = Cr, Mo, W, n = 4) containing only one ligand bridge can also be obtained. In the former compounds complete or partial substitution of amino groups by HBr was carried out, to give $(CO)_4M$ *cis*-$[Br_2P(CH_2)_4PBr_2]$ (M = Cr, Mo), and $(CO)_4W$ *cis*-$[Et_2N(Br)$-$P(CH_2)_4P(Br)NEt_2]$, respectively. By the same method $(CO)_5CrBr_2PPBr_2Cr$-$(CO)_5$, in which P_2Br_4 is stabilized by complex formation, was obtained from $(CO)_5Cr(Et_2N)_2PP(NEt_2)_2Cr(CO)_5$. The NMR, IR and mass spectra of the complexes are discussed.

Introduction

Bifunctional aminophosphanes $(Et_2N)_2P(CH_2)_nP(NEt_2)_2$ (I) (n = 1—10) were prepared by us [1,2] for a systematic study of the coordination behaviour of these new bifunctional ligands in metal(0) complexes: Coordination with formation of mono- or binuclear complexes should be possible depending on the value of n. Several methods by which amino groups of coordinated monofunctional phosphanes can be exchanged for halogen have been described [3—9]. In the case of the free ligands I, substitution-reactions, e.g. with HBr and PCl_3, were easily carried out, giving halogenophosphanes $X_2P(CH_2)_nPX_2$ [10]. It was of interest to know whether substitution was also possible in case of coordinated I, and this would lead to complexes containing reactive ligands we needed for other work. Previous attempts to prepare such compounds had

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failed, as bifunctional dibromophosphanes proved to react only very reluctantly with metal carbonyls [1].

For similar reasons we included $(Et_2N)_2PP(NEt_2)_2$ (II) in our investigations, hoping to be able to replace Et_2N groups by bromine in the coordinated ligand and thus to stabilize the still unknown P_2Br_4 by complexation. Disproportionation had been prevented in this way in the case of R(X)PP(X)Br (R = aryl, X = Br, I) [11,12].

Metal(0) complexes with bifunctional aminophosphanes (I)

Mononuclear complexes and binuclear compounds containing I

If *cis*-activated $(CO)_4Cr$ NBD (NBD = Norbornadiene) is reacted with Ia—Id in equimolar quantities, intramolecular coordination occurs leading to the octahedral *cis* compounds IIIa—IIId, the constitution of which can be deduced from their physical properties (Table 1). In accord with their local C_{2v} symmetry, *cis*-substituted tetracarbonyl complexes show 4 absorptions in the CO stretching region [13,14]. These are also found in III, which proved to be monomeric in benzene.

With Ie—Ig only binuclear octahedral complexes VI could be isolated from the reaction mixture. Thus, notwithstanding *cis* activation in the starting complex, intermolecular coordination via *trans* positions had taken place with the long-chain biphosphanes. Some properties of VI are listed in Table 1. The IR spectrum shows one strong and two weak absorptions in the CO-stretching region, consistent with octahedral *trans*-substituted carbonyl complexes. Though only one strong absorption is expected for *trans*-substituted complexes with D_{4h} symmetry, two IR-forbidden absorptions of weak intensity are often observed because of deviations from microsymmetry [15].

Solutions of III and VI show only one singlet in their $^{31}P\{^1H\}$ spectra, which is shifted strongly to low field compared with the resonance of the corresponding free ligand ($\Delta\delta(P)$ values in Table 1). These singlets are also the only ones observed for the reaction mixture obtained in preparation of mononuclear

TABLE 1

SPECTROSCOPIC DATA AND MOLECULAR WEIGHTS OF THE COMPLEXES III AND VI

Compound	$\delta(P)$ [a] (ppm)	$\Delta\delta(P)$ [b] (ppm)	$\nu(CO)$ [c] (cm^{-1})				Molecular weight (±4%)
IIIa	113.4	32.1	2009m,	1923s,	1904s,	1892s	536
IIIb	168.4	77.7	2010s,	1918s,	1901s,	1889s	540
IIIc	171.4	83.6	2026w,	1945s,	1938s,	1875s	562
IIId	155.7	67.8	2006m,	1914s,	1895s,	1889s	567
VIa	173.5	85.6	1935w,	1894w,	1872s		1144
VIb	173.0	85.0	1931w,	1886w,	1876s		1186
VIc	173.4	85.3	1924w,	1887w,	1878s		1229
VId	173.5	85.4	1923w,	1885w,	1878s		1239
VIe	173.4	85.1	1944w,	1893w,	1885s		1281
VIf	173.1	84.9	1943w,	1890w,	1881s		1300

[a] 10% in CH_2Cl_2. [b] $\Delta\delta(P) = |\delta(P)(\text{free ligand}) - \delta(P)(\text{coordinated ligand})|$. [c] In pentane.

TABLE 2

SPECTROSCOPIC DATA AND MOLECULAR WEIGHT OF COMPLEXES WITH LIGAND Id

Compound	$\delta(P)$ [a] (ppm)	$\Delta\delta(P)$ [f] (ppm)	$\nu(CO)$ [b] (cm^{-1})				EI/MS [c]	Molecular weight (±4%)
VIIa	148.7	60.8	2062w,	1955sh,	1947vs,	1938s	790(5)	806
VIIb	133.2	45.3	2072w,	1988vw,	1956vs,	1945s	882(1)	872
VIIc	114.6 [d]	26.7	2073vw,	1955sh,	1939vs,	1928m	1054(9)	1070
IV	137.1	49.2	2017m,	1923s,	1906s,	1890s	616(3)	608
V	119.7 [e]	31.8	2017m,	1918m,	1896s,	1891sh	702(9)	705

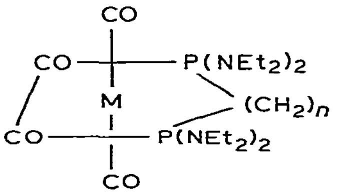
[a] 10% in CH_2Cl_2. [b] In pentane. [c] $M^{+\cdot}$ (%). [d] $J(^{183}W—^{31}P)$ 281 Hz. [e] $J(^{183}W—^{31}P)$ 276 Hz. [f] $\Delta\delta(P) = |\delta(P)\ (\text{free ligand}) - \delta(P)\ (\text{coordinated ligand})|$.

complexes IIIa—IIIc ($n = 3$) and binuclear compounds VIb—VIf ($n = 6$). In the case of the bifunctional aminophosphanes (Id: $n = 4$; Ie: $n = 5$) of intermediate chainlength n the reaction mixtures show another much weaker resonance, which may be attributed to binuclear and mononuclear species, respectively, simultaneously formed in small amounts; isolation of these was not attempted.

$(Et_2N)_2P(CH_2)_nP(NEt_2)_2$

(I)

I	a	b	c	d	e	f	g	h	i	j
n	1	2	3	4	5	6	7	8	9	10



(III M = Cr)

III	a	b	c	d
n	1	2	3	4

(IV M = Mo, n = 4;
V M = W, n = 4)

As far as ^1H NMR spectra are concerned there are no significant differences between those of the free and coordinated ligands apart from broadening of resonances. In particular the N—CH_2 resonance no longer shows fine structure after coordination. This effect and the low field shift in the $^{31}P\{^1H\}$ spectra show that coordination of the ligands in III and VI occurs via phosphorus, not nitrogen [16].

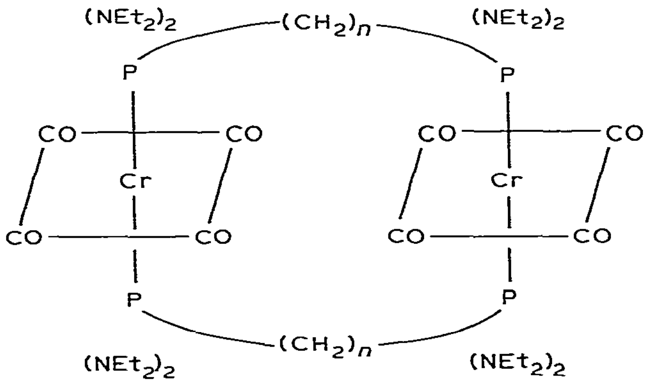
While $\Delta\delta(P)$ values (Table 1) are found to be fairly constant in VI (~85 ppm) they range from 32.1—83.6 ppm in compounds III. According to Garrou [17,18] chelate formation contributes to the low field shift; this contribution is maximal for 5- and 6-membered rings and lower for smaller and greater rings [19]. As this also applies to III this provides additional evidence for chelate formation in these complexes and ligand bridges in VI. The increased stability of the 5- and 6-membered chelate ring compounds IIIb, IIIc with regard to ligand exchange was evident from $^{31}P\{^1H\}$ measurements; while for a mixture of IIIb, IIIc, Ia and Id no additional resonance is observed, a mixture of IIIa, IIId, Ib and Ic shows singlets corresponding to all the possible exchange products.

Mo- and W-complexes $(CO)_4M$ *cis*-$[(Et_2N)_2P(CH_2)_4P(NEt_2)_2]$ (IV M = Mo, V M = W) were prepared in good yield by heating equimolar quantities of $M(CO)_6$ with Id for several hours (Table 2).

To summarize, intramolecular coordination with formation of *cis*-coordinated chelate rings is the preferred process when Ia—Id are reacted with metal carbonyls in equimolar quantities. Complexes containing 5- or 6-membered rings are the most stable; Steric and electronic effects of amino groups opposing *cis* coordination in aminophosphane complexes [20] are obviously outweighed by the chelate effect. This is not so with ligands Ie—Ij, containing longer chains, $(CH_2)_n$ ($n > 4$), from which binuclear complexes with two bridging ligands in *trans* positions are mainly formed.

Binuclear complexes with a single ligand bridge

Complexes of type VII $(CO)_5M[Et_2N)_2P(CH_2)_4P(NEt_2)_2]M(CO)_5$ (VIIa M = Cr; VIIc M = W) with only one ligand bridge were obtained when the ratio ligand/metal carbonyl was reduced from 1/1 to 1/2 or less. Thus, binuclear VIIa and VIIc could be isolated from the reaction mixture, when Id and $(CO)_5M$-



(VI)

VI	a	b	c	d	e	f
n	5	6	7	8	9	10

$(CO)_5M(Et_2N)_2P(CH_2)_4P(NEt_2)_2M(CO)_5$

(VII)

(VIIa M = Cr ; VIIb M = Mo ; VIIc M = W)

(THF) were reacted in molar ratio 1/2, mononuclear chelate complexes IIId and V being the other main products. In spite of change in stoichiometry and activation of only one octahedral site in the starting complexes the tendency for chelate formation is apparently so strong, that the binuclear compounds VIIa and VIIc are formed in only 50% yield.

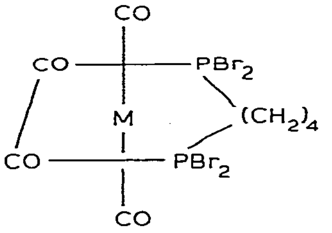
The constitution of VII was deduced from analytical data, molecular weight, and spectroscopic measurements (Table 2). Their EI-mass spectra show the molecule ion $LM_2(CO)_{10}^{+\cdot}$ and fragments corresponding to successive loss of all CO. The base peak can be assigned to $LM(CO)_4^{+\cdot}$, as is the case with other binuclear carbonyl complexes [21].

While the IR spectra show 4 absorptions in the CO stretching region as expected for carbonyls with pseudo-C_{4v}-symmetry [13], there is only a singlet in the $^{31}P\{^1H\}$ spectra accompanied by the two ^{183}W satellites in the case of VIIc.

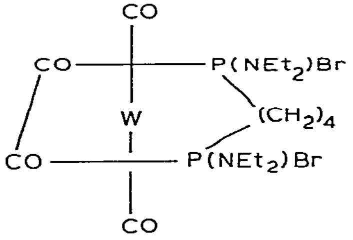
Cleavage of P—N bonds in coordinated bifunctional aminophosphane Id by HBr

Attempts to react $Br_2P(CH_2)_4PBr_2$ (Id) [10] with $M(CO)_6$ (M = Cr, Mo, W) or $(CO)_4CrNBD$ under various conditions gave only very small amounts of $(CO)_4M$ *cis*-$[Br_2P(CH_2)_4PBr_2]$ VIII (VIIIa M = Cr; VIIIb M = Mo; VIIIc M = W) [1].

VIIIa and VIIIb were, however, easily prepared from the corresponding aminophosphane complexes IIId and IV by condensing gaseous HBr into solutions of the two latter compounds. This procedure had already proved to be very efficient in converting the free ligands into the corresponding bromo-compounds $Br_2P(CH_2)_nPBr_2$ [10]. While the free ligands reacted with HBr even at —90° C, exchange of Et_2N groups in the coordinated ligands occurred only above —40° C, showing their reduced reactivity. Conversion of aminophosphane metal carbonyls into the corresponding bromophosphane complexes with HBr was previously reported [4—6].



(VIII)



(IX)

(VIIIa M = Cr ; VIIIb M = Mo)

In case of V only partial exchange of Et_2N groups for bromine was achieved by this method, the product being $(CO)_4W$ *cis*-$[Et_2N(Br)P(CH_2)_4P(Br)NEt_2]$ (IX). As the latter complex contains two chiral P atoms, formation of *meso*- and *rac*-IX is expected in its synthesis, and the $^{31}P\{^1H\}$ spectrum of IX shows two resonances of nearly equal intensity at δ(P) 141.4 and 140.7 ppm (toluene, 10%; $J(^{183}W—^{31}P)$ 295 Hz), which may be assigned to the two stereoisomers.

An alternative structure for IX, containing the unsymmetrical ligand $Br_2P(CH_2)$-$P(NEt_2)_2$, can be excluded because of the small difference between the two observed δ(P) values.

It should be mentioned, that compared with the free ligand (δ(P) 187.4 ppm [1,2]) the $^{31}P\{^1H\}$ resonance is shifted to low field in the chromium complex VIIIa (δ(P) 190.1 ppm) and to high field in the molybdenum compound VIIIb (δ(P) 150.0 ppm, all values in toluene, 10%).

Stabilisation of diphosphorus tetrabromide in $(CO)_5CrBr_2PPBr_2Cr(CO)_5$ (XI)

Reaction of II with $(CO)_5CrTHF$ gave $(CO)_5Cr(Et_2N)_2PP(NEt_2)_2Cr(CO)_5$ (X) in 20% yield. Treatment of X with HBr gave complete exchange of Et_2N groups and XI was isolated in 90% yield. Thus, diphosphorus tetrabromide was stabilized for the first time, the disproportionation of this highly unstable compound into PBr_3, lower phosphorus bromides, and phosphorus is prevented by coordination [11].

Experimental

All operations were performed under nitrogen using standard glass ware. Nitrogen, solvents and SiO_2 were purified and dried by common procedures. Photolyses: Normag-photoreactor, TQ 150 Hanau; Photochemical lamp located in the water-jacketed inner tube. IR: Perkin—Elmer IR 283. FT ^{31}P NMR: Bruker Physik HX 90 R, external standard 85% H_3PO_4, positive values of the shifts, δ(P), are to low field.

MS: Varian MAT 311 A, EI, 70 eV. Molar mass: Cryoscopically in benzene, Cryoscope of Fa. Knauer, Berlin. C, H, N analyses: Perkin—Elmer Analyzer 263, Inst. of Pharmacy, Univ. Düsseldorf.

Starting materials: $(CO)_4CrNBD$ and $(CO)_4MoNBD$ were prepared by literature procedures [22]. The synthesis of I will be described elsewhere [1,2].

Tetrakis(diethylamino)diphosphane II was obtained by a procedure [23] modified as follows:

Tetrakis(diethylamino)diphosphane (II)

A solution of bis(diethylamino)chlorophosphane (95 mmol) in 100 ml toluene is added dropwise at 0°C during 4 h to a suspension of sodium (26 mmol) in 400 ml toluene. The mixture is then stirred for 2 h and allowed to warm slowly to room temperature. The solution is filtered and the residue washed twice with 30 ml toluene. The combined filtrate and washings are evaporated under reduced pressure and the residual yellow oil is distilled. Yield 12.2 g (73%), b.p. 67—69°C (10^{-3} Torr). ^{31}P NMR (neat): δ 82.5 ppm. EI/MS: m/z 350 ($M^{+\cdot}$ 2%); lit. [24]: b.p. 132°C (3 mm), ^{31}P NMR: δ 86.5 ppm; lit. [25]: b.p. 70°C/0.02 mm.

General procedure for the preparation of tetracarbonyl-cis-1,n-organdiyl-bis-[bis(diethylamino)phosphane]chromium(0) IIIa—IIId

A solution of $(CO)_4CrNBD$ (5 mmol) and bis-aminophosphane Ia—Id (5 mmol) in 200 ml pentane is stirred for 24 h at room temperature, then the solvent and unreacted starting materials are removed under reduced pressure by gentle

TABLE 3

TETRACARBONYL-*cis*-1,*n*-ORGANDIYL-BIS[BIS(DIETHYLAMINO)PHOSPHANE]CHROMIUM(0) (IIIa—IIId)

Compound	Formula Molecular weight	M.p. (°C) Yield (%)	EI/MS [a]	Analyses (Found (calcd.) (%))				
				C	H	N	P	Cr
(IIIa) -1,1-methandiyl-	$C_{21}H_{42}CrN_4O_4P_2$	67—68	528	46.7(47.7)	7.9(8.0)	10.3(10.6)	11.7(11.7)	9.6(9.8)
	528.3	83	22					
(IIIb) -1,2-ethandiyl-	$C_{22}H_{44}CrN_4O_4P_2$	89—90	542	48.0(48.7)	8.2(8.2)	10.0(10.3)	11.0(11.4)	9.3(9.6)
	542.6	77	18					
(IIIc) -1,3-propandiyl-	$C_{23}H_{46}CrN_4O_4P_2$	111—112	556	49.2(49.6)	8.3(8.3)	10.0(10.1)	11.0(11.1)	9.3(9.3)
	556.6	68	9					
(IIId) -1,4-butandiyl-	$C_{24}H_{48}CrN_4O_4P_2$	113—114	570	50.3(50.5)	8.5(8.5)	9.7(9.8)	10.9(10.9)	9.0(9.1)
	570.6	80	3					

[a] $M^{+\bullet}$ (%).

warming. The residue is dissolved in 20 ml pentane and the solution filtered through a layer of SiO_2 (2 cm, 16 mm ⌀, 70—235 mesh ASTM). After 50 h at —35°C pale yellow crystals are formed, and these are filtered off at —30°C and dried in vacuum at room temperature.

Octacarbonyl-μ-trans-bis[1,n-organdiyl-bis(bis(diethylamino)phosphane)]dichromium(0) (VI)

Preparation of VIa and VIb: A solution of $(CO)_4CrNBD$ (5 mmol) and an equimolar amount of Ie or If in 100 ml pentane is stirred for 40 h at room temperature. The mixture is then filtered and the filtrate concentrated to 20 ml under reduced pressure. Addition of 80 ml acetone to the boiling concentrate gives a precipitate of pale yellow crystals, and the suspension is stirred for 2 h at room temperature. The crystals are filtered off and dried in vacuum.

Preparation of VIc—VIf:

A solution of $(CO)_4CrNBD$ (5 mmol) and Ig—Ij (5 mmol) in 100 ml pentane is stirred for 12 h at room temperature. The solution is evaporated to dryness under reduced pressure, and the oily residue is dissolved in a small volume of CH_2Cl_2. The solution is filtered through a layer of SiO_2 (2.0 cm, ⌀ 16 mm, 70—235 mesh ASTM) and kept for 5 days at —35°C. The yellow crystals formed are filtered off and dried in vacuum.

Decacarbonyl-μ-1,4-butandiyl-bis[bis(diethylamino)phosphane]dichromium(0) (VIIa)

A solution of Id (11.8 mmol) in 30 ml THF was added dropwise during 2 h to a solution of $Cr(CO)_5 \cdot THF$ prepared from $Cr(CO)_6$ (24.3 mmol) in 380 ml THF (UV irradiation, 5 h). The solvent and unreacted $Cr(CO)_6$ are removed under reduced pressure at room temperature and the residue is dissolved in 20 ml THF. The solution is chilled to —35°C, and the solid formed is recrystallized from pentane at —35°C. Pale-yellow crystals, yield 4.1 g (44%); m.p. 155—156°C (dec.). (Found: C, 44.8; H, 6.2; N, 6.8; P, 8.0; Cr, 13.1. $C_{30}H_{48}Cr_2N_4O_{10}P_2$ calcd.: C, 45.6; H, 6.1; N, 7.1; P, 7.8; Cr, 13.2%; molec. wt. 790.7).

Decacarbonyl-μ-1,4-butandiyl-bis[bis(diethylamino)phosphane]dimolybdenum(0) (VIIb)

The phosphane Id (3.2 mmol) is added dropwise during 10 min to a solution of $Mo(CO)_6$ (45.5 mmol) in 60 ml toluene at 90°C. The mixture is heated under reflux for 8 h, then filtered. The filtrate is evaporated to dryness and unreacted starting materials are removed from the residue at room temperature in vacuum. Crystallization from pentane/CH_2Cl_2 (1/1, v/v) at —20°C gives colourless crystals, m.p. 148°C (dec.), yield 1.4 g (50%). (Found: C, 40.0; H, 5.4; N, 6.3; P, 7.0; Mo, 21.6. $C_{30}H_{48}N_4Mo_2O_{10}P_2$ calcd.: C, 41.0; H, 5.5; N, 6.4; P, 7.1; Mo, 21.8%; molec. wt. 878.6).

Decacarbonyl-μ-1,4-butandiyl-bis[bis(diethylamino)phosphane] ditungsten(0) (VIIc)

A solution of Id (7.4 mmol) in 25 ml THF is dropwise added during 2 h to a

TABLE 4

OCTACARBONYL-μ-*trans*-BIS[1,*n*-ORGANDIYL-BIS(BIS(DIETHYLAMINO)PHOSPHANE] DICHROMIUM(0) (VIa—VIf)

Compound	Formula Molecular weight	M.p. (°C) Yield (%)	Analyses (Found (calcd.) (%))				
			C	H	N	P	Cr
(VIa) -1,5-pentandiyl-	$C_{50}H_{100}Cr_2N_8O_8P_4$ 1169.3	156—158 (dec.) 80	50.7(51.4)	8.7(8.6)	9.2(9.6)	10.5(10.6)	8.6(8.9)
(VIb) -1,6-hexandiyl-	$C_{52}H_{104}Cr_2N_8O_8P_4$ 1197.3	155—157 (dec.) 87	51.8(52.2)	8.5(8.8)	9.1(9.4)	10.3(10.4)	8.8(8.7)
(VIc) -1,7-heptandiyl-	$C_{54}H_{108}Cr_2N_8O_8P_4$ 1225.4	158—160 (dec.) 68	52.3(52.9)	8.7(8.9)	9.2(9.1)	10.2(10.1)	8.6(8.5)
(VId) -1,8-octandiyl-	$C_{56}H_{112}Cr_2N_8O_8P_4$ 1253.4	140—141 (dec.) 75	52.6(53.7)	8.8(9.0)	8.8(8.9)	10.0(9.9)	8.3(8.3)
(VIe) -1,9-nonandiyl-	$C_{58}H_{116}Cr_2N_8O_8P_4$ 1281.5	118—119 (dec.) 54	53.3(54.4)	9.0(9.1)	8.4(8.7)	9.6(9.7)	8.2(8.1)
(VIf) -1,10-decandiyl-	$C_{60}H_{120}Cr_2N_8O_8P_4$ 1309.6	84—85 (dec.) 47	54.3(55.0)	9.0(9.2)	8.5(8.6)	9.3(9.5)	8.1(7.9)

solution of $W(CO)_5 \cdot THF$, prepared from $W(CO)_6$ (15.1 mmol) and 380 ml THF (UV irradiation, 5.5 h). The solvent and unreacted $W(CO)_6$ are removed during 10 h under vacuum at room temperature and the residue is purified by chromatography (column 200 × 40 mm, CH_2Cl_2/pentane (1/4 v/v), SiO_2 70—235 mesh ASTM). The yellow fraction is concentrated to 20 ml and kept for several hours at —20°C. The yellow crystals formed are dried in vacuum. Further product can be obtained by chilling the filtrate again after concentrating it to a volume of 10 ml. Total yield 3.5 g (45%), m.p. 64—66°C (dec.) (Found: C, 33.8; H, 4.4; N, 5.2; P, 5.7; W, 34.7. $C_{30}H_{48}N_4O_{10}P_2W_2$ calcd.: C, 34.2; H, 4.6; N, 5.3; P, 5.9; W, 34.9%; molec. wt. 1054.4).

Tetracarbonyl-cis-1,4-butandiyl-bis[bis(diethylamino)phosphane] molybdenum-(0) (IV)

A solution of $Mo(CO)_6$ (4.5 mmol) and Id (4.5 mmol) in 45 ml toluene is refluxed for 9 h. The solvent is evaporated and the oily residue dissolved in a mixture of 18 ml pentane and 3 ml CH_2Cl_2. The solution is kept at —35°C for 24 h to give ivory-coloured crystals, which are dried in vacuum. Yield 2.11 g (77%), m.p. 120—121°C. (Found: C, 46.6; H, 7.9; N, 9.6; P, 9.9; Mo, 15.5. $C_{24}H_{48}MoN_4O_4P_2$ calcd.: C, 46.9; H, 7.9; N, 9.1; P, 10.1; Mo, 15.6%; molec. wt. 614.6).

Tetracarbonyl-cis-1,4-butandiyl-bis[dibromophosphane] chromium(0) (VIIIa)

About 2 l (room temperature, normal pressure) of gaseous HBr are condensed by cooling with liquid nitrogen into a solution of IIId (6.7 mmol) in 500 ml toluene. The mixture is warmed to —100°C and then brought slowly with stirring to room temperature. After filtration the solution is evaporated and the residue crystallized from CH_2Cl_2 at —35°C. Yellow crystals, dec. 200°C; yield 3.5 g (87%). (Found: Cr, 8.5; P, 10.4; Br, 52.8%; molec. wt. 608 ± 3%. $C_8H_8Br_4CrO_4P_2$ calcd.: Cr, 8.6; P, 10.3; Br, 53.1%; molec. wt. 601.7).

Tetracarbonyl-cis-1,4-butandiyl-bis[bis(diethylamino)phosphane] tungsten(0) (V)

A solution of $W(CO)_6$ (3.6 mmol) and Id (3.6 mmol) in 40 ml toluene is refluxed for 60 h. The purification is as for VI, yellow needles, m.p. 136—137°C (dec.). Yield 1.92 (76%). (Found: C, 40.8; H, 6.9; N, 8.0; P, 8.9; W, 26.1. $C_{24}H_{48}N_4O_4P_2W$ calcd.: C, 41.0; H, 6.9; N, 8.0; P, 8.8; W, 26.2%; molec. wt. 702.5).

Tetracarbonyl-cis-1,4-butandiyl-bis(dibromophosphane)molybdenum (0) (VIIIb)

Preparation analogous to VIIIa from 1 l of gaseous HBr and IV (4.2 mmol) in 350 ml toluene. Yellow crystals, dec. 200°C. Yield 1.7 g (63%). (Found: Mo, 14.7; P, 9.8; Br, 49.5%; molec. wt.: 648 ± 3%. $C_8H_8Br_4MoO_4P_2$ calcd.: Mo, 14.9; P, 9.6; Br, 49.5%; molec. wt. 645.5).

Tetracarbonyl-cis-1,4-butandiyl-bis[diethylaminobromophosphane] tungsten(0) (IX)

Preparation analogous to VIIIa from 0.5 l gaseous HBr and V (2.1 mmol) in 200 ml toluene. Yellow crystals from pentane/CH_2Cl_2 (1/1 v/v) at —35°C, m.p.

76—78°C (dec.), yield 1.3 g (86%). (Found: C, 26.5; H, 3.9; N, 3.9; P, 8.4; W, 25.5; Br, 22.2%; molec. wt. 701 ± 3%. $C_{16}H_{28}Br_2N_2O_4P_2W$ calcd.: C, 26.8; H, 3.9; N, 3.9; P, 8.6; W, 25.6; Br, 22.3%; molec. wt. 718.0).

Decacarbonyl-µ-tetrakis(diethylamino)diphosphane-dichromium(0) (X)

Freshly distilled tetrakis(diethylamino)diphosphane (12.0 mmol) is dropwise added during 10 min to a solution of $(CO)_5Cr\cdot THF$, prepared from $Cr(CO)_6$ (24.1 mmol) and 380 ml THF (UV irradiation, 5.5 h). The solution is stirred for 1 h then the solvent and unreacted $Cr(CO)_6$ are removed under vacuum at room temperature during 5 h. The oily brown residue is chromatographed (column 200 X 40 mm, pentane/CH_2Cl_2 (10/1 v/v), SiO_2 70—235 mesh ASTM). The pale yellow fraction is taken to dryness at room temperature and recrystallized from pentane at —35°C. Yellow crystals, m.p. 42—43°C (dec.), yield 1.8 g (20%). (Found: C, 42.7; H, 6.2; N, 7.6; P, 8.4; Cr, 14.2. $C_{26}H_{40}Cr_2N_4O_{10}P_2$ calcd.: C, 42.5; H, 5.5; N, 7.6; P, 8.4; Cr, 14.3%; molec. wt. 734.6).

Decacarbonyl-µ-tetrabromodiphosphane-dichromium(0) (XI)

The preparation of XI from X and its spectroscopic data are described in [11]. (Found: C, 16.1; Br, 41.3; Cr, 13.9; P, 8.0. $C_{10}Br_4Cr_2O_{10}P_2$ calcd.: C, 15.7; Br, 41.7; Cr, 13.6; P, 8.1%; molec. wt. 765.7).

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