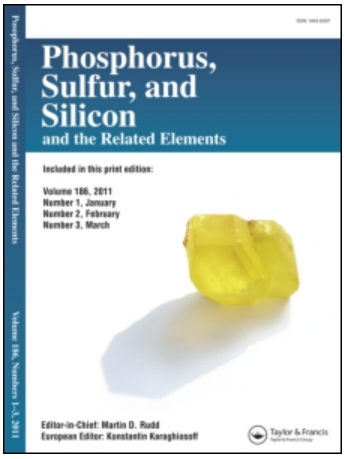

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COMPLEXES COBALT DINITROSYLE-AMINOPHOSPHONITE: CARACTERISATION DE 3 MODES DE COORDINATION

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COMPLEXES COBALT DINITROSYLE-AMINOPHOSPHONITE : CARACTERISATION DE 3 MODES DE COORDINATION.

D. Ballivet-Tkatchenko*, M. Bonnet*, R. Faure** et H. Loiseleur**.
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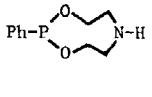
**Laboratoire de Chimie analytique II, 43, Bld du 11 novembre 1918, 69621 Villeurbanne cédex, France.

L'aminophosphonite cyclique 1 réagit avec $[Co(NO)_2Cl]_2$ pour former 3 types d'adduit, 2, 3 et 4. La caractérisation par diffraction des rayons-X montre 3 modes de coordination distincts. La première interaction entre 1 et l'ion Co s'effectue par formation de la liaison Co-P. Puis s'il existe des sites de coordination supplémentaire autour d'un ion Co, une deuxième liaison se forme avec le bras amine du ligand 1 pour donner soit 1 chélatant, 3, soit 1 pontant, 4, selon les conditions réactionnelles. Le complexe 4 est le premier exemple, caractérisé par rayons-X, du composé 1 à caractère pontant.



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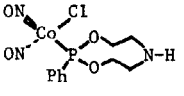

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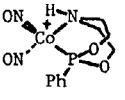

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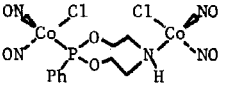
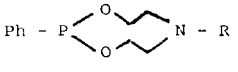


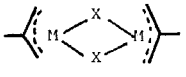
4

COMPORTEMENT DES LIGANDS AMINOPHOSPHONITES CYCLIQUES VIS-A-VIS DE COMPLEXES ALLYLIQUES DU NICKEL ET DU PALLADIUM [1].

S. AGBOSSOU, M.C. BONNET, A. STORECK et I. TKATCHENKO - Institut de Recherches sur la Catalyse, 2, avenue Albert Einstein - 69626 Villeurbanne Cédex - FRANCE

La réaction des ligands 1 et 2 qui se différencient par la présence d'un bras amine secondaire ou tertiaire, avec les complexes allyliques 3 et 4 conduit à des composés dont la structure et la réactivité dépendent de la stoechiométrie (1:1 à 4:1), du substituant sur le bras amine et de la nature du métal employé.





1 R = H ; 2 R = Me 3 M = Pd ; X = Cl 4 M = Ni ; X = Br

Les complexes du nickel avec 1 sont plus stables que ceux du palladium ; inversement, les complexes du nickel avec 2 sont moins stables. De plus, le ligand 1 présente un hydrogène "non innocent" susceptible d'être éliminé au cours du processus de complexation pour conduire à un complexe phosphoranure, ce qui étendrait au groupe VIII le comportement de ce ligand déjà observé en chimie de coordination des métaux de transition du groupe VI [2].

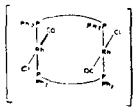
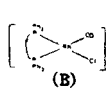
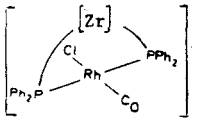
1. Travaux subventionnés par le CNRS

2. J. WACHTER, B.F. MENTZEN et J.G. RIESS, Angew. Chem., Int. Ed. Engl. 1981, 20, 284.
F. JANNEAUX, A. GRAND et J.G. RIESS, J. Amer. Chem. Soc., 1981, 103, 4272.

UTILISATION DE LA DIPHOSPHINE η-$Cp_2Zr(CH_2PPh_2)_2$ DANS LA FORMATION DU COMPLEXE HETEROBIMETALLIQUE [Zr-Rh] : FORMATION INATTENDUE DU COMPLEXE MONOMERE TRANS-[η-$Cp_2Zr(CH_2PPh_2)_2(Rh(CO)Cl)$], par Robert CHOUKROUN et Danièle GERVAIS, Laboratoire de Chimie de Coordination du CNRS, 205, route de Narbonne, 31400 TOULOUSE, France.

Le phosphinométhyl zirconium η-$Cp_2Zr(CH_2PPh_2)_2$ est utilisé pour préparer, par complexation avec $(Rh(CO)_2Cl)_2$, le complexe hétérobinucléaire [η-$Cp_2Zr(CH_2PPh_2)_2(Rh(CO)Cl)$] (composé monomère).

Au contraire des composés du rhodium(I) avec des diphosphines $>P(CH_2)_nP<$ décrits récemment dans la littérature qui sont dimères avec des phosphines trans par rapport au rhodium (fig. A) et du composé monomère cis [Rh(CO)Cl(dppe)] ($^2J(P\text{-}P) = 34$ Hz) (fig. B), le spectre $^{31}P\{^1H\}$ du complexe monomère [Zr-Rh] enregistré à température variable, montre l'inéquivalence des atomes de phosphore liés en trans sur l'atome de rhodium (spectre de forme ABX : $\delta = 37{,}4$ et $24{,}0$ ppm ; $^1J(Rh\text{-}P) = 136$ et 137 Hz ; $^2J(P\text{-}P) = 316$ Hz). La non équivalence des atomes de phosphore apparaît sur le modèle moléculaire. (fig. C)

(A)  (B)   (C)

REACTIONS OF INORGANIC PHOSPHATES WITH PLATINUM(II).

Rathindra N. Bose and Richard D. Cornelius, Department of Chemistry. Wichita State University, Wichita, Kansas 67208 U.S.A.

The reactions of orthophosphate, pyrophosphate, and triphosphate ions with cis-$Pt(NH_3)_2Cl_2$ and $Pt(NH_3)_2(H_2O)_2^{2+}$ have been examined. Platinum blues form when $Pt(NH_3)_2(H_2O)_2^{2+}$ reacts with any of these inorganic phosphates. These blues decompose entirely over a period of 24 hours in aqueous solution, but the platinum blue containing triphosphate ion has been isolated in solid form. The reactions of $Pt(NH_3)_2Cl_2$ have been monitored by UV-visible spectrophotometry and by phosphorus-31 NMR. With pyrophosphate and triphosphate ions, the rapid initial reaction follows the rate law $k_{obsd} = k_1 + k_2[\text{phosphate}]$ where k_1 is equal to the rate of aquation under identical conditions. The value of k_2 is smaller than for any other nucleophiles reported in the literature. A subsequent, slower reaction may be due to chelation by the phosphate ligand. Both monodentate and bidentate complexes have been detected by phosphorus-31 NMR.

STABILISATION DE CYCLOPENTADIENYL-HALOGENO-PHOSPHINES PAR COMPLEXATION, B. Deschamps et F. Mathey, Equipe CNRS-SNPE, 2-8 rue H. Dunant, 94320 Thiais (France)

Les cyclopentadiényl-halogeno-phosphines $CpPX_2$, Cp_2PX ou $\begin{matrix}Cp\\R\end{matrix}\!\!>\!P-X$ sont instables, sauf pour X=F. Nous sommes parvenus à les isoler sous forme de complexes stables par coordination de la paire libre du phosphore sur le tungstène pentacarbonyle. Le schéma de synthèse est le suivant :

$$PX_3 \text{ (ou } RPX_2) \xrightarrow{CpTl} CpPX_2 \text{ (ou } \begin{matrix}Cp\\R\end{matrix}\!\!>\!PX) \xrightarrow{W(CO)_5\text{-THF}} \underset{W(CO)_5}{CpPX_2} \text{ (ou } \begin{matrix}R\\Cp\end{matrix}\!\!>\!P\!\rightarrow\!W(CO)_5)$$

Les halogénophosphines libres, non isolables, ont tout de même pu être observées in situ par RMN ^{31}P. Complexées par $W(CO)_5$, elles ont été isolées et une étude analytique et spectroscopique complète en a été effectuée.
L'obtention de ces composés permet de relancer la chimie des cyclopentadiényl-phosphines dans le but de synthétiser de nouvelles molécules phosphorées originales. Nous avons abordé à la fois les réactions sur le Cp (Diels Alder) et sur le phosphore (substitutions de l'halogène).

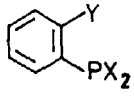
THE COORDINATION BEHAVIOR OF o-SUBSTITUTED PHENYLPHOSPHINES AS LIGANDS IN METAL CARBONYL COMPLEXES

Beatrix Kottwitz and Klaus Diemert, Institut für Anorganische Chemie und Strukturchemie I Universitätsstr. 1, D-4000 Düsseldorf 1

Several ligands of type 1 have been prepared. Depending on the synthetic route and substituents X and Y ligands 1 show mono- and/or bifunctional behavior towards $M(CO)_6$ (M = Cr, W) leading to compounds 2 and cis-3.

Coordination proceeds stepwise starting with phosphorus. Chelation by coordination of Y follows as second step and can be easily cancelled by subsequent addition of other ligands (e.g. CO, PR_3).

The orientation of the vinylic group in chelates 3 is discussed on the basis of the ^{13}C-NMR-spectrum of 3 (M = Cr, X = NEt_2, Y = $-CH{=}CH_2$).



1

Y = $-OCH_3$, $-CH{=}CH_2$
X = Cl, NEt_2

$M(CO)_5 \cdot$ 1 (2)

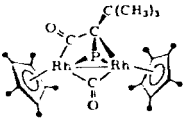
$M(CO)_4 \cdot$ 1 (3)

M = Cr, W

ADDITION OF AN ALKYLIDYNEPHOSPHINE TO METAL METAL MULTIPLE BONDS

W.A. Herrmann, M.L. Ziegler, G. Becker, W. Kalcher, G.W. Kriechbaum, C. Pahl, and C.T. Wagner, Inst. f. Anorg. Chemie d. Univ. Niederurseler Hang D-6000 Frankfurt a.M. 50 and Pfaffenwaldring 55 D-7000 Stuttgart 80

Two years ago some of us [1] have reported the synthesis of 2,2-dimethylpropylidynephosphine via a catalytic decomposition of [2,2-dimethyl-1-(trimethylsiloxy)propylidene]-trimethylsilylphosphine. Elucidating the chemical properties of this remarkable compound it has been treated with transition metal complexes as $\{[\eta^5\text{-}C_5(CH_3)_5\text{-}\mu\text{-}CO]Rh\}_2$ and $[(\eta^5\text{-}C_5H_5)(CO)_2Mo]_2$ containing a metal metal multiple bond. Analogous to reactions of alkynes the addition products 1 and 2 were isolated. An X-ray structure determination of the dimetalla-phospha-tetrahedrane derivative 2 shows a P-C distance of 172 pm which is characteristic for a P-C double bond [2], see also [3].



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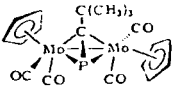


2

[1] G. Becker, G. Gresser, and W. Uhl, Z. Naturforsch. 36b, 16 (1981).
[2] G. Becker, W.A. Herrmann, W. Kalcher, G.W. Kriechbaum, C. Pahl, C.T. Wagner, and M.L. Ziegler, Angew. Chem. 95, 417 (1983).
[3] J.C.T.R. Burckett-St. Laurent, P.B. Hitchcock, H.W. Kroto, M.F. Meidine, and J.F. Nixon, J. Organomet. Chem. 238,C82 (1982).

THE INTERACTION OF SODIUM TETRAHYDROBORATE AND SODIUM CYANOTRIHYDROBORATE WITH Co(II) AND Ni(II) SALTS IN THE PRESENCE OF BIDENTATE PHOSPHINES.

D.G. Holah, A.N. Hughes, N.I. Khan, and S. Maciaszek, Department of Chemistry, Lakehead University, Thunder Bay, Ontario, Canada P7B 5E1, and V. Magnuson, Department of Chemistry, University of Minnesota - Duluth, Duluth, Minnesota 55812, U.S.A.

The reactions of Co(II) chloride with $NaBH_4$ and of Ni(II) chloride and perchlorate with $NaBH_3CN$ in the presence of the bidentate phosphines $Ph_2P(CH_2)_nPPh_2$ (n = 1-5), cis $Ph_2PCH{=}CHPPh_2$ and trans $Ph_2PCH{=}CHPPh_2$ are reported. The Co(II) system gives the Co(I) products $Co_2(phosphine)_2Cl_2$ (chloride bridged), $Co(BH_4)(phosphine)$, and $CoH(phosphine)_2$ in the sequence listed. The tetrahydroborato complexes (formed when n = 3 or 5) are dimeric and demonstrate a previously unknown type of tetrahydroborate coordination in which two tetrahydroborate units bridge two metal ions which are further bridged by two phosphines in a plane perpendicular to the plane defined by the metal and boron atoms. The hydrides are mainly (except for n = 1) 5-coordinate trigonal bipyramids with apical hydride. The behaviour of the Ni(II) system depends greatly upon the phosphine chain length. Thus, $Ph_2PCH_2PPh_2$ gives mainly the air-sensitive binuclear Ni(I) systems $Ni_2(CN)(BH_3CN)(phosphine)_2$, $Ni_2(CN)_2(phosphine)_3$, and $Ni_2(CN)_2(phosphine)_2$. The first two of these contain bridging phosphines and a Ni(I)-Ni(I) bond while the third is a Ni(I)-Ni(I) system containing chelating phosphines and terminal CN groups. The sequence of product formation is discussed. For $Ph_2PCH_2CH_2PPh_2$, the products are mainly binuclear Ni(II) systems and some of these are highly unusual in structure. Thus, $[Ni_2(BH_3CN)_3(phosphine)_2]X$ contains 3 bridging BH_3CN^- groups and other bridged species are formed.

NOVEL PHOSPHANES CONTAINING A SIGMA BONDED PENTAMETHYLCYCLOPENTADIENYL-DICARBONYLIRON GROUP

W. Malisch, W. Angerer, I. Kuhn and W. S. Sheldrick
Institut für Anorganische Chemie der Universität Würzburg,
Am Hubland, D-8700 Würzburg (Germany)

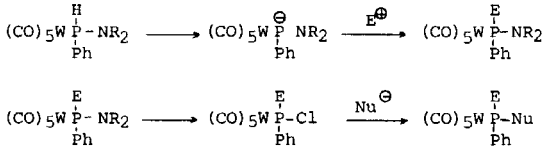
The reaction of $Na[Fe(CO)_2C_5Me_5]$ with Ph_2PCl, PCl_3, $PhPCl$, $tBuPCl_2$ leads to novel iron substituted phosphanes $C_5Me_5(CO)_2Fe\text{-}PR_2$ [R = Ph (Ia), Cl (Ib)] and $C_5Me_5(CO)_2Fe\text{-}P(R)Cl$ [R = Ph (IIa), tBu (IIb)]. (Ia) can be easily oxidized with elemental sulphur to $C_5Me_5(CO)_2Fe\text{-}PPh_2(S)$ or transformed to the adduct $C_5Me_5(CO)_2Fe\text{-}PPh_2\text{-}BH_3$ (III) by the interaction with $BH_3\cdot THF$. The stucture of the borane adduct (III) will be presented and its reactivity discussed in detail[1]. In addition the chemical behaviour of the phosphanes towards various phosphor donors and on photolysis will be reported.

1) W. Angerer, W. Malisch and W. S. Sheldrick, Organometallics, submitted for publication.

QUELQUES APPLICATIONS DU POTENTIEL SYNTHETIQUE DES COMPLEXES $(CO)_5W[PPh(H)NR_2]$ (I)

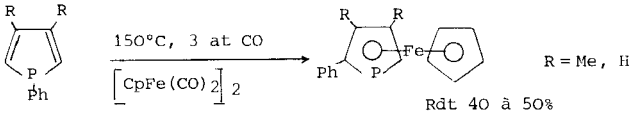
A. Marinetti et F. Mathey, Equipe CNRS-SNPE, 2-8 rue H. Dunant, 94320 Thiais (France)

Les N-phénylphosphinamides (I) stabilisées par complexation présentent la double réactivité d'une liaison PH et d'une liaison PN, transformable en PCl. Leurs réactions successives avec une espèce électrophile et une espèce nucléophile ont comme résultat la synthèse de molécules phosphorées très variées et normalement difficilement accessibles. Le schéma réactionnel général est le suivant :



REACTIVITE DES PHOSPHOLES-2H SUR LES METAUX CARBONYLES, F. Mercier et F. Mathey, Equipe CNRS-SNPE, 2-8 rue H. Dunant, 94320 Thiais (France)

Sachant que les phényl-1-phospholes sont susceptibles vers 140°C de se transposer en phospholes-2H, il est possible d'envisager une nouvelle voie d'accès aux phosphamétallocènes comparable dans son principe à la synthèse des métallocènes. Celle-ci ferait intervenir un processus de π complexation du phosphole-2H après expulsion d'un proton. Mais pour atteindre ce stade, il est nécessaire d'empêcher la complexation σ classique du métal sur le phosphole de départ avant que celui-ci ne subisse la migration 1,5 du phényle. Dans le cas de la complexation avec les métaux carbonyles, il est possible d'empêcher cette complexation en retardant le départ de CO en travaillant sous pression d'oxyde de carbone. Les premiers résultats obtenus dans ce sens semblent confirmer nos hypothèses. Nous avons alors appliqué ce concept à la synthèse optimisée des phosphaferrocènes :

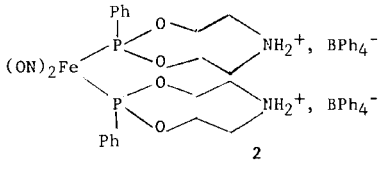


Disposant de ces complexes en quantité plus abondante que par le passé, nous avons étudié leurs propriétés rédox.

REACTIVITY OF AMINOPHOSPHANE IRON NITROSYL COMPLEXES TOWARDS O_2 AND BORON DERIVATIVES. L. Mordenti, J.L. Roustan, F. Tomi, M. Postel, J.G. Riess. Laboratoire de Chimie Minérale Moléculaire, Equipe associée au CNRS. Université de Nice, Parc Valrose, 06034 NICE-Cedex.

The trimetallic iron complex $(NO)_2Fe|PhP(OCH_2CH_2)_2NHFe(NO)_2I|_2$, **1**, reacts with $NaBPh_4$ in EtOH to give the ionic complex **2** and/or **3**; in the latter the NH group of the open tautomeric form of $PhP\overline{H(OCH_2CH_2)_2}\overline{N}$, **4**, is bonded to BPh_3. Complex **3** is formed by decomposition of **2**, one phenyl group being released as Ph-H at room temperature.
The complexes **2** and/or **3**, depending upon the experimental conditions, were also obtained by allowing **4** to react with dimer $|Fe(NO)_2I|_2$, **5**, and then with $NaBPh_4$ (in EtOH) or BPh_3 (in CH_2Cl_2).

The reaction of $O_2$with **1** caused the disappearance of the νNO vibrations and the appearance of νNO_2 absorptions in the IR. The system converts phosphanes to phosphane oxides. Oxidation of organic substrates is under study, together with the preparation of new adducts and attempts to identify the active species; the aim being to create a catalytic oxidation cycle such as that shown in **5**.



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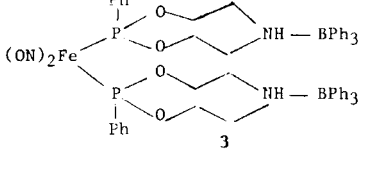

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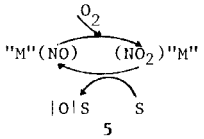
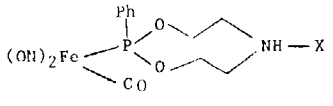
S=substrat;M=metal



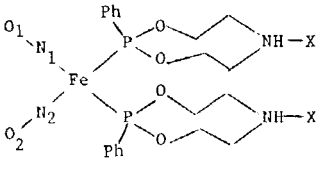
5

SYNTHESIS AND STRUCTURE OF AMINOPHOSPHANE IRON NITROSYL COMPLEXES. L. Mordenti, G. Le Borgne, J.L. Roustan, J.G. Riess. Laboratoire de Chimie Minérale Moléculaire, Equipe de Recherche Associée au CNRS. Université de Nice, Parc Valrose, 06034 NICE Cedex.

The bicyclic phosphorane, $PhP\overline{H(OCH_2CH_2)_2N}$, **1**, in its monocyclic open tautomeric form, displaces one or two carbonyl groups from $Fe(CO)_2(NO)_2$ to yield the P-only bonded adducts $(ON)_2Fe(CO)|PhP(OCH_2CH_2)_2NH|$, **2**, and $(NO)_2Fe|PhP(OCH_2CH_2)_2NH|_2$, **3**.
These adducts further react through their NH sites with $|Fe(NO)_2I|_2$, **4** to yield the di- and trimetallic complexes $(ON)_2Fe(CO)|PhP(OCH_2CH_2)_2NH||Fe(NO)_2I|$, **5** and $(ON)_2Fe|PhP(OCH_2CH_2)_2NH|_2|Fe(NO)_2I|_2$, **6**.
The X-Ray crystal structure determination was used to rationalize the origin of the 3300 cm^{-1} absorption observed in the solid state IR spectra of **3**, similar to the ν NH found for the chelating (P and N bonded) ligand **1** in cationic complexes. The formulation **3** was confirmed (δ:Fe-N = 1.64Å, Fe-P = 2.19Å, N_1-O_1 = 1.176Å, N_2-O_2 = 1.194Å, angles : Fe-N-O = 177.7°, N_1-Fe-N_2 = 128.3°, O_1-Fe-O_2 = 128.0°, P_1-Fe-P_2 = 98.47°) and evidence was found for intermolecular hydrogen bonding.



2.3:X=no substituent
5.6:X=Fe(NO)2I



PHOSPHITE COMPLEXES OF COBALT RHODIUM AND IRIDIUM, S.I. Klein and J.F. Nixon, School of Chemistry and Molecular Sciences, University of Sussex, Brighton, BN1 9QJ, England.

Synthetic routes to the fluxional complexes $[M(P(O)(OMe)_2)(P(OMe)_3)_4]$ (M = Co, Rh, Ir) will be described and their differing behaviour towards H_2 and protic acids will be discussed. The crystal and molecular structure of $[IrH(P(O)(OMe)_2)(P(OMe)_3)_4SnMe_2Cl_2]^+$ $[Me_2SnCl_3]^-$ will be presented. Dinuclear complexes of the type $[M_2L_8]$, (L = phosphite) have been synthesised and studied in solution by ^{31}P NMR spectroscopy. The synthesis of the novel stable paramagnetic complex $[Rh(P(O^iPr)_3)_4]$ and its e.p.r. spectrum will be discussed.

STRUCTURE AND REACTIVITY OF t-PHOSHPINE RHODIUM COMPLEX HYDROFORMYLATION CATALYSTS:
Alexis A. Oswald, Dan E. Hendriksen, Rodney V. Kastrup, Joseph C. Merola, Edmund J. Mozeleski and John C. Reisch*, Exxon Research and Engineering Co., P. O. Box 45, Linden, NJ 07036, and Exxon Chemical Co.*, P. O. Box 241, Baton Rouge, LA 70821

Electronic and steric effects on t-phosphine rhodium complex catalyzed, selective, low pressure 1-butene hydroformylation were studied. The catalysis results were correlated with the structure and equilibrium concentration of the desired stable intermediates in such complex plus free t-phosphine catalyst systems:

$(Ph_2PR)_3Rh(CO)H$ and $(Ph_3P)_3Rh(CO)H$ Ph = phenyl; R = alkyl

Comparative studies of various new alkyldiarylphosphine and the recently commercialized triphenylphosphine complex catalysts showed that, the new catalyst complexes are similarly highly selective but more stable. They require a higher temperature for activation, and do not undergo dephenylation during continuous product flashoff type hydroformylations.

Electronic effects of substituents on the γ-carbon of the ethyl group of Ph_2PR ligands did not significantly affect the new catalyst systems. However, steric crowding by branching of the β and particularly the α-carbon did decrease their selectivity for n-aldehyde products and increased their reactivity.

Sufficient understanding of the steric factors in Ph_2PR rhodium complex chemistry was gained to allow the design of new selective complex catalysts for hydroformylation at different temperatures and CO partial-pressures.

STUDY OF THE CHEMICAL BOND IN $(C_6H_5)_{3-n}PX_n$ (X = H, Cl, Br, I; n = 0-3) AND CORRESPONDING CHROMIUM CARBONYL COMPLEXES.

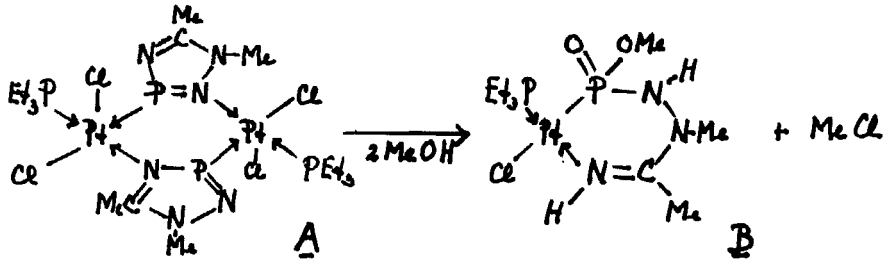
L. VERDONCK, E. VINCENT.
Laboratory for General and Inorganic Chemistry-B, Krijgslaan 281, B-9000 GENT-BELGIUM.

The chemical bond in the $(C_6H_5)_{3-n}PX_n$ (X = H, Cl, Br, I; n = 0-3) and $(C_6H_5)_{3-n}PX_nCr(CO)_5$ derivatives is studied by NMR, XPS and IR-spectroscopy.
The experimental parameters are shown to be governed by the concomitant influence of inductive, mesomeric and steric effects of the phosphine ligand. For X = halogen, they are mainly determined by the inductive effect of the $(C_6H_5)_{3-n}PX_n$ group, while for X = H, the steric requirements of the phosphine ligand are imperative.
Furthermore, the fact that independent physical parameters such as, the I.R. CO frequency, $\nu(CO)A_1(eq)$, the C^{13} NMR chemical shift $\delta^{13}C(CO)$ and the XPS C_{1s} and $O_{1s}(CO)$ binding energies, are mutually correlative, is strong evidence for the importance of the $(d_{Cr} \rightarrow \pi^*_{CO})\pi$ back-bonding concept.

ZERO- AND DIVALENT PLATINUM COMPLEXES OF TRI- AND DIAZAPHOSPHOLES,

K. Vrieze, J.G. Kraaykamp, G. van Koten, D.M. Grove and A. Schmidpeter*
Anorganisch Chemisch Lab., University of Amsterdam, Nwe Achtergr. 166, Amsterdam;
*Inst. für Anorganische Chemie der Universität, Meiserstrasse 1, 8000 München 1.

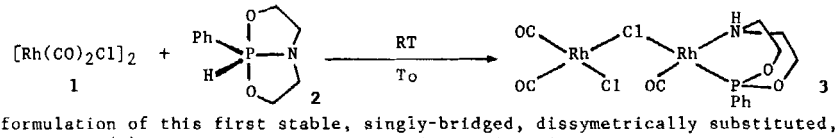
Diazaphospholes MeN-N=CMe-CH=P (D) and triazaphospholes P=N-NMe-CMe=N (T) react with $Pt(PPh_3)_4$ to afford $(PPh_3)_3PtL_1$ (L = D,T) in which the phospholes probably coordinate via P as suggested by the crystal structure determination of $(PPh_3)_3PtT$. Coordination of T to Pt(II) leads to interesting reactivity of the coordinated ligand in methanol. NMR (^1H, ^{31}P, ^{13}C, ^{195}Pt) and crystallographic investigations show the conversion of A into B in methanol, which proceeds via two mono-nuclear intermediates involving ring opening, addition of two MeOH and oxidation of P^{III} to P^V.



A B

SYNTHESIS, MOLECULAR STRUCTURE AND REACTIVITY OF A SINGLY BRIDGED, DISSYMETRICALLY SUBSTITUTED, DINUCLEAR RHODIUM(I) ADDUCT. J. Wachter, Inst. für Anorganische Chemie, Universitätstrasse 31, D-8400 Regensburg, F. Jeanneaux, P. Brun, J. Riess, Lab. Chimie Minérale Moléculaire, ERA-C.N.R.S., Univ. Nice, Parc Valrose, 06034 Nice-cedex, G. Le Borgne, Lab. de Cristallographie, Univ. Rennes, Av. Général Leclerc, 35042 Rennes-cedex.

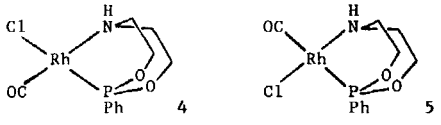
Compound 3 was isolated in near quantitative yields in the absence of light by allowing equimolar amounts of dimer 1 and bicyclic aminophosphorane 2 to react according to :



1 2 3

The formulation of this first stable, singly-bridged, dissymetrically substituted, diamagnetic Rh(I) complex was attested by elemental analysis, IR, NMR and mass spectrometry, and X-ray diffraction.

Reaction of 3 with a second equivalent of 2 gives, in addition of the antisymbiotic isomer 4 usually formed, the unstable non-antisymbiotic isomer 5.



4 5

The reaction of 3 with small donor molecules, including CO, SO_2 and ethynes will also be discussed.

METAL DITHIOPHOSPHINATES IN PREPARATION OF ION SPECIFIC RESINS AND HPLC TRACE ANALYSIS.

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Institut für Anorganische Chemie und Strukturchemie I, Universitätsstr. 1
D-4000 Düsseldorf 1

Metal dithiophosphinates are employed in model tests for optimising the specifity of ion exchanging resins and for multielement trace analysis. Crosslinking copolymerisation of vinylic substituted metal dithiophosphinates $[R_2PS_2]M/n$ (e.g. R = p-CH_2=CH-C_6H_4) with common comonomers yields resins, from which most of the metal can be eluated. When treated with aqueous solutions of different metal ions, the products thus obtained show a distinct preference for the metal originally incorporated into the polymer. Thus, fixing well defined metal complexes in a polymer matrix makes available "tailored" coordination sites in a rigid arrangement which will be preserved even when the central ions are removed. This is possibly a new route for synthesis of ion specific resins.
HPLC proves to be a sensitive method for detecting geometric isomers in solutions of planar or octahedral complexes $[RR'PS_2]M/n$ and for the separation of metals via their dithiophosphinates (e.g. Pd,Pt,Ru,Rh and Ir). Moreover, metals in trace amounts can be determined simultaneously with this method after extraction of aqueous solutions with $(C_2H_5)_2PS_2Na$.

STRUCTURES OF THE LIGAND NONAMETHYLIMIDODIPHOSPHORAMIDE(NIPA) AND THE COMPLEX $[UO_2(NIPA)_2EtOH](ClO_4)_2$, STUDIED BY X-RAY DIFFRACTION AND NMR.

K.Bokolo, L.Rodehüser, P.Rubini, and J.-J.Delpuech, Laboratoire de Chimie Physique Organique, ERA CNRS 222, Université de Nancy I, France.
A.Courtois, E.Elkaïm, and J.Protas, Laboratoire de Minéralogie Cristallographie, ERA CNRS 162, Université de Nancy I, France.

Bidentate neutral diphosphoramides form stable complexes with a variety of metal cations. They are equally interesting as extractants for metal salts from dilute aqueous solutions. The ligand NIPA yields tris-chelate complexes with most of the di- and tervalent spherical cations; in the case of the linear UO_2^{2+} ion, however, complexes with one, two, or three NIPA molecules can be isolated depending on the conditions of preparation. The species obtained in the presence of ethanol when starting from $UO_2(ClO_4)_2$ is the title compound. An analysis of the solid by X-ray diffraction reveals the chelate nature of the two NIPA molecules and a pentagonal arrangement of the four P=O oxygens and the oxygen of the ethanol in a plane perpendicular to the O=U=O unit. The ^{31}P n.m.r. spectra of the compound dissolved in an inert solvent (CD_3NO_2, CD_2Cl_2) prove that the configuration of the solid complex is retained in solution. The structure of the ligand NIPA itself, on the other hand, changes from the trans-configuration in the solid state (O-O distance 4.635 Å) to a cis-configuration in the complex (O-O distance 2.805 Å) by rotation around the P-N-P bond.