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Palladium(I) phosphido-bridged dinuclear derivatives with phosphite ligands

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Abstract—New mono-phosphido-bridged cationic derivatives of dipalladium(I) have been prepared by reacting $[Pd_2(\mu - PBu'_2)(PPh_3)_3]BF_4$ (2)BF₄, with P(OR)₃ (R=Me, Et, Ph). Under a large excess of the entering phosphite, all the PPh₃ molecules terminally bonded to the central $Pd_2(\mu - PBu'_2)$ core can be substituted, yielding $[Pd_2(\mu - PBu'_2)\{P(OR)_3\}_4]BF_4$, $[(4a)BF_4, R=Me; (4b)BF_4, R=Et and (4c)BF_4, R=Ph]$. The intermediate mixed-ligand complex $[Pd_2(\mu - PBu'_2)(PPh_3)\{P(OPh)_3\}_2]BF_4$, (5)BF₄, was isolated in the reaction with P(OPh)₃. Moreover, the reactions of the new complexes with CO, isoprene and CS₂ were investigated and compared to the corresponding reactions of the phosphine-substituted complexes. © 1998 Elsevier Science Ltd. All rights reserved

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The chemistry of phosphido-bridged palladium(I) dinuclear derivatives was rather unexplored until a few years ago [1]. Our group is involved in a systematic study of this field [2-7], and has shown that the secondary phosphine-bridged $[Pd_2(\mu - PBu_2^t)]$ $(\mu - PBu_2^tH)(PBu_2^tH)_2]BF_4$, (1)BF₄ [3], can be employed as the precursor of a series of mono-phosphido-bridged cationic derivatives of general formula $[Pd_2(\mu, PBu_2^t)(PR_3)_n]BF_4$, [4] with n depending on the steric demand of the phosphine ligand (n=3,R = Ph [(2)BF₄]; n = 4, R = Me [(3a)BF₄], R = Et $[(3b)BF_4]$ or $R_3 = Cy_2H$, $[(3c)BF_4]$; see Scheme 1). Both (1) BF_4 and its derivatives with other phosphines have shown an interesting reactivity; they can be used as a source of still rare examples of terminally bonded Pd(I) carbonyls [3b, 5] or show cooperation of the two metal centers in the coordination of polyunsaturated molecules as isoprene [5, 6] or CS_2 [4b, 7]. We now report the synthesis of new members of this family, bearing phosphites terminally bonded to the central $[Pd_2(\mu - PBu'_2)]^+$ core, and compare their reactivity with that given by their phosphine analogues.



EXPERIMENTAL

General and instrumental

All reactions were performed under an atmosphere of purified nitrogen or carbon monoxide by using standard Schlenck techniques. Solvents were dried by

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standard procedures and distilled under nitrogen prior to use. Deuterated solvents were used as purchased and stored on molecular sieves under an inert atmosphere. $[Pd_2(\mu - PBu'_2)(PPh_3)_3]BF_4$, (2)BF_4, was prepared as previously described [4b]. IR spectra were recorded with a Perkin-Elmer FT-IR 1725X spectrophotometer and NMR spectra with a Varian Gemini 200BB spectrometer, frequencies were referenced to the residual signal of the deuterated solvent (¹H, ¹³C) and to external 85% H₃PO₄ (³¹P). The progress of the reactions was monitored by means of ³¹P{¹H} NMR spectroscopic analyses of small samples of a reaction mixture, after adding a few drops of C₆D₆ for the lock signal capture and the field homogeneity optimization operations.

Preparation of $[Pd_2(\mu - PBu'_2){P(OMe)_3}_4]BF_4$, (4a) BF_4 . Trimethyl phosphite (0.16 mL, 1.44 mmol) was added to a red acetone (10 mL) solution of (2) BF_4 (179 mg, 0.145 mmol). The solution turned quickly orange; after 15 min most of the solvent was evaporated and *n*-hexane (20 mL) was added, causing the precipitation of a yellow powder which was filtered off, washed with *n*-hexane, and *vacuum* dried (95 mg, 70% yield).

Elem. Anal. Calcd for $C_{20}H_{54}BF_4P_5Pd_2$: C, 25.5, H, 5.78. Found: C, 25.6, H, 5.80%. ³¹P{¹H} NMR (CDCl₃, 298 K): δ (ppm) 345.5 (tm, ²*J*_{PP} \approx 282, 46 Hz, μ -PBu'₂), 136.2 (dm, ²*J*_{PP} \approx 280 Hz, *P*(OMe)₃ trans to μ -P), 127.2 (m, *P*(OMe)₃ cis to μ -P). ¹H NMR (CDCl₃, 298 K): δ (ppm) 3.65 (m, 36 H, OCH₃), 1.35 (d, ³*J*_{HP} = 14.2 Hz, 18 H, PC(CH₃)₃). IR (Nujol, KBr): 1028 s, br (ν _{BF}) cm⁻¹.

Preparation of $[Pd_2(\mu - PBu'_2){P(OEt)_3}_4]BF_4$, (**4b**) BF_4 . Triethyl phosphite (0.37 mL, 2.16 mmol) was added to a red acetone (15 mL) solution of (**2**) BF_4 (266 mg, 0.216 mmol). The solution turned quickly orange; after 30 min most of the solvent was evaporated after which *n*-hexane (25 mL) was added, causing the precipitation of a yellow powder. The suspension was left overnight at -30° C, the solid filtered off, washed with *n*-hexane, and *vacuum* dried (158 mg, 66% yield).

Elem. Anal. Calcd for $C_{32}H_{78}BF_4O_{12}P_5Pd_2$: C, 34.6, H, 7.09. Found: C, 34.8, H, 6.99. ³¹P{¹H} MMR (Acetone-d₆, 298 K): δ (ppm) 345.6 (tm, ²*J*_{PP} \approx 280, 50 Hz, μ –PBu^{*i*}₂), 137.2 (dm, ²*J*_{PP} \approx 280 Hz, *P*(OEt)₃ trans to μ -P), 123 (m, *P*(OEt)₃ cis to μ -P). ¹H NMR (CDCl₃, 298 K): δ (ppm) 3.9 (br s, 24 H, OCH₂CH₃), 1.3 (overlapping m, 54 H, OCH₂CH₃ + PC(CH₃)₃). IR (Nujol, KBr): 1034 s, br (v_{BF}) cm⁻¹.

Preparation of $[Pd_2(\mu - PBu'_2){P(OPh)_3}_4]BF_4$, (**4***c*)*BF*₄. Triphenyl phosphite (1.71 mL, 6.52 mmol) was added to a red CH₂Cl₂ (15 mL) solution of (**2**)*BF*₄ (80 mg, 0.065 mmol). The color of the solution turned quickly orange; after 15 min 2/3 of the solvent were evaporated and Et₂O (20 mL) was added, causing the precipitation of an orange powder which was filtered, washed with Et₂O, and vacuum dried (88 mg, 80% yield).

Elem. Anal. Calcd for C₈₀H₇₈BF₄O₁₂P₅Pd₂: C, 57.0,

H, 4.66. Found: C, 57.6, H, 4.66. ³¹P{¹H} NMR (CDCl₃, 298 K): δ (ppm) 360.0 (tt, ²J_{PP} \approx 240, 46 Hz, μ -PBu^t₂), 118.0 (dm, ²J_{PP} = 240 Hz, *P*(OPh)₃ trans to μ -P), 103 (m, *P*(OPh)₃ cis to μ -P). ¹H NMR (CDCl₃, 298 K): δ (ppm) 7.2 (m, 60 H, OC₆H₅), 1.3 (d, ³J_{HP}=15 Hz, 18 H, PC(CH₃)₃). IR (Nujol, KBr): 1055 s, br (ν _{BF}) cm⁻¹.

Preparation of $[Pd_2(\mu - PBu'_2)(PPh_3){P(OPh_3)_2}]BF_4$, (5)*BF*₄. Triphenyl phosphite (4.07 mL, 15.5 mmol) was added to a red CH₂Cl₂ (10 mL) solution of (**2**)BF₄ (327 mg, 0.26 mmol). The color of the solution turned quickly orange; after 15 min most of the solvent was evaporated and Et₂O (30 mL) was added, causing the precipitation of an orange powder which was filtered, washed with Et₂O, and *vacuum* dried (220 mg, 64% yield).

Elem. Anal. Calcd for $C_{62}H_{63}BF_4O_6P_4Pd_2$: C, 56.1, H, 4.78. Found: C, 58.5, H, 5.05. ³¹P{¹H} NMR (acetone-d₆, 298 K): δ (ppm) 374.2 (ddd, ²J_{PP}=195, 102, 70 Hz, μ -PBu'₂), 124.2 (ddd, ²J_{PP}=102, 37 Hz, ³J_{PP}=363 Hz, *P*(OPh)₃), 113.6 (ddd, ²J_{PP}=70, 14 Hz, ³J_{PP}=363 Hz, *P*(OPh)₃), 26.8 (ddd, ²J_{PP}=195, 37 Hz, ³J_{PP}=14 Hz), the spectrum shows other minor signals (see Results and Discussion) due to other compounds which justify the low purity found in elemental analysis, attempted purification by column chromatography led to decomposition. ¹H NMR (CDCl₃, 298 K): δ (ppm) 7.1 (m, 45 H, PC₆H₅+OC₆H₅), 1.4 (d, ³J_{HP}=14.6 Hz, 18 H, PC(CH₃)₃). IR (Nujol, KBr): 3040 (ν =_{CH}), 1588, 1486 (ν _C=_C), 1055 s, br (ν _{BF}) cm⁻¹.

Reactions of $(4a,b)BF_4$ with CS_2 A 10-fold excess of CS_2 was added by syringe to a CDCl₃ solution (0.5 mL) of $(4a)BF_4$ (15 mg, 0.0159 mmol) or $(4b)BF_4$ (18 mg, 0.0162 mmol). The orange solutions turned quickly yellow and were analyzed by ³¹P{¹H} NMR spectroscopy (see Results and Discussion).

Reactions of $(4a,b)BF_4$ with isoprene A 10-fold excess of isoprene was added by syringe to a CDCl₃ solution (0.5 mL) of $(4a)BF_4$ (16 mg, 0.017 mmol) or $(4b)BF_4$ (19 mg, 0.0171 mmol). The orange solutions turned quickly yellow and were analyzed by ³¹P{¹H} NMR (see Results and Discussion).

Reactions of (4a,b) BF_4 with *CO* Carbon monoxide was bubbled into orange CDCl₃ solutions of complex (4a) BF_4 or (4b) BF_4 (*ca* 30 mg/mL). A faint bleaching of the starting colour was observed and the solutions were analyzed by ³¹P{¹H} NMR spectroscopy which exhibited only the resonances of the reagents. The IR spectra of the solutions exhibited medium-weak v_{CO} absorptions around 2070 cm⁻¹.

RESULTS AND DISCUSSION

The unsaturated triphenylphosphine derivative $[Pd_2(\mu - PBu'_2)(PPh_3)_3]BF_4$, (2)BF₄ [4b], proved to be a suitable precursor to phosphite substituted complexes. When acetone or methylene chloride solu-

tions of $(2)BF_4$ were reacted at room temperature with an excess of the appropriate phosphite, the corresponding persubstituted derivatives (eq 1) were formed and isolated as yellow microcrystalline solids in satisfactory to good yields (67-80%). The reactions were fast and clean when at least a 10-fold excess of the alkyl phosphite was employed; in the case of triphenyl phosphite a higher excess of the ligand was necessary. The new complexes analyzed nicely for the composition $[Pd_2(\mu - PBu_2^t) \{P(OR)_3\}_4]BF_4$, $[(4a)BF_4, R = Me; (4b)BF_4, R = Et and (4c)BF_4,$ R = Ph] and, as inferred by the analysis of ³¹P NMR spectra (see below), retain the usual [4a] structure exhibited by the analogous phosphine derivatives, with two palladium centers in a distorted square planar geometry sharing a bridging phosphido ligand and the metal-metal bond.

the P-nuclei trans and cis to X, the bridging phosphorus. Due to the magnetic non-equivalence of the couples AA' and BB', the spectrum cannot be interpreted with simple first order approximations, and can be quite complex. In general, the lines within the multiplets are no longer directly correlated to the values of ${}^{2}J_{AX}$, ${}^{2}J_{BX}$ and ${}^{2}J_{AB}$, but to combinations of these coupling constants and of ${}^{3}J_{AA'}$, ${}^{3}J_{BB'}$ and ${}^{3}J_{AB'}$. When the differences (in Hertz) between the values of δ_A , δ_B and δ_X are much larger than coupling constants values, as in the case of the phosphine derivatives [4a], the spectrum is still relatively simple and easily simulated. The large downfield shift of δ_A and δ_B which occurs when phosphites are employed in place of the phosphines (around 100 ppm) approaches them to δ_x ; the spin system is better defined as AA'BB'C and give rise to an extreme complication of the spec-



The ${}^{31}P{\{1H\}}$ NMR spectrum of (4b)BF₄ is shown in Scheme 1, with the numbering scheme.

This particular framework of phosphorus atoms $(Pd_2P_5 \text{ planar core with } C_{2v} \text{ symmetry})$ constitutes an AA'BB'X spin system where A and B are, respectively,

tra; none of the nine independent variables of the spin system can be easily extracted from the spectrum. Due to this difficulty only some spectral features were reproduced in the simulation with a satisfactory approximation. This is particularly true for the low



Fig. 1. ³¹P{¹H} NMR spectrum (acetone-d₆, 293 K) of $[Pd_2(\mu - PBu'_2) \{P(OEt)_3\}_4]BF_4$ (4b)BF₄, with the numbering scheme.

field signal due to μ -P, which highly resembles the signal given by the corresponding phosphorus [4a] of $[Pd_2(\mu - PBu'_2)(PR_3)_4]BF_4$ (R = Me, Et), and allows an approximate evaluation of δ_C , ${}^2J_{AC}$ and ${}^2J_{BC}$, respectively found at *ca* 345.5 ppm, 282 and 46 Hz for (**4a**)BF₄, *ca* 345.6 ppm, 280 and 50 Hz for (**4b**)BF₄ and *ca* 360 ppm, 240 and 46 Hz for (**4c**)BF₄. These values confirm the approximately planar disposition of the Pd₂(μ -P)P₄ core, with two *pseudo-trans* and two *pseudo-cis* (compared to μ -P) phosphite ligands.

¹H NMR spectra are easily interpreted and give the expected integral ratio between the various types of nuclei.

With lower $P(OR)_3/(2)BF_4$ ratios we observed the formation of mixtures of products arising from the progressive stepwise substitution of the three triphenylphosphine molecules contained in $(2)^+$. The number of observed intermediates, of general formula $[Pd_2(\mu - PBu_2^t)(PPh_3)_{(3-n)} \{P(OPh)_3\}_n]BF_4$, is generally high, since different geometrical isomers were observed for a given value of n. Therefore very complex mixtures were formed in most cases but one. In fact, when $(2)BF_4$ was reacted with a 10-fold excess of P(OPh)₃ one of these intermediates can be isolated sufficiently pure and readily identified as $[Pd_2(\mu - PBu_2^t)(PPh_3) \{P(OPh)_3\}_2]BF_4$, (5)BF₄. Its ${}^{31}P{}^{1}H$ NMR spectrum is quite simple and shows a doublet of doublets of doublets (${}^{2}J_{PP} = 195$, 70, 102 Hz) at 374.2 ppm for the bridging phosphide (P₁); the remaining three P nuclei give resonances at 26.8 ppm (ddd, $J_{PP} = 195$, 37, 14 Hz), assigned to the phosphorus (P₂) of a PPh₃ molecule(for its high field position) *trans* to μ -P (for the large $J_{PP} = 195$) and at 124.2 ($J_{PP} = 363$, 37, 102 Hz) and 113.6 ($J_{PP} = 363$, 70, 14 Hz), respectively assigned to P₃ of the phosphite on the tricoordinated palladium center and to P₄ of the phosphite *cis* to the phosphine molecule.



The assignment of the latter two resonances has been made by considering that the coupling to P₁ should be minor (70 Hz) when the angle P–Pd–P1 approaches 90° (P₄), and increase (102 Hz) when this angle becomes wider (P₃). Larger values of J_{PP} were observed for phosphite-phosphite or phosphite-phosphine couples with respect to the corresponding phosphine-phosphine couples of the structurally related cation (2)⁺. The exceedingly high value of ${}^{3}J_{P3P4}$ = 363 Hz is probably due to a nearly linear dis-



position of the $(PhO)_{3}P-Pd-Pd-P(OPh)_{3}$ fragment; the corresponding constant was found at 135 Hz in $(2)^{+}$ [4b].

The purity of the samples of $(5)BF_4$ is not high (*ca*

³¹P{¹H} NMR spectra of the solutions show that in both cases the same type of equilibrium given by the cations (1)⁺ and (2)⁺ has established, yielding the CS₂ adducts (6a)BF₄ and (6b)BF₄ (eq 2). The spectra of



80%) and small amounts of other intermediates were observable in the spectrum but not identified due to severe overlapping of the weak signals. Well separated signals were observed only in the phosphide region, where two weak ddd appear at 369.8 (${}^{2}J_{\rm PP}$ =155, 52, 98 Hz) and 355.5 ppm (${}^{2}J_{\rm PP}$ =220, 75, 61 Hz) suggesting for these derivatives the same type of skeleton assigned to (5)⁺.

Reactivity of the cations $(4a,b)^+$. The availability of the new complexes allowed us to investigate the influence of the substitution with phosphites on the reactivity of this class of derivatives. We decided to use as tests the reactions with CS₂, isoprene and carbon monoxide, which had previously been investigated for the corresponding phosphine substituted derivatives [3b, 4–7].

Reactions with CS_2 . We knew that carbon disulfide reacts with the cations $(1)^+ \cdot (3)^+$ yielding the corresponding adducts (see Scheme 2) [4b]; these exhibited an unprecedented coordination mode of the CS_2 molecule, with a central planar $Pd_2P_3(CS_2)$ core. One or two phosphine molecules are displaced from the starting complex; in one case (PMe₃) this can behave as a nucleophile toward the metal bonded carbon disulfide molecule [8].

An orange $CDCl_3$ solution of the alkyl phosphite derivatives (4a)BF₄ or (4b)BF₄ turns immediately yellow when reacted with a 10-fold excess of CS₂. The these species are very simple, as those given by the corresponding phosphine derivatives [4b], and consist of a high field triplet and a low field doublet coupled by a small ${}^{2}J_{PP(cis)}$; these parameters were found at 417.6, 130.1 ppm and 27 Hz for (**6a**)BF₄ and 354.2, 133.5 ppm and 24 Hz for (**6b**)BF₄.

A significant difference between the reactions given by $(4a)BF_4$ and $(4b)BF_4$ concerns the position of the equilibrium. In the former case this is shifted toward the reagents: with also larger amounts of CS₂ the resonances of the cation $(4a)^+$ are well visible in the spectrum, although severely broadened by exchange processes. On the contrary, the reaction with $(4b)BF_4$ is shifted toward $(6b)BF_4$ and, with a 10-fold excess of CS₂, the resonances assigned to $(4b)^+$ have nearly completely disappeared from the spectrum.

Reactions with isoprene. Isoprene is another potentially bidentate ligand which was shown to react with the phosphine cations $(1)^+ - (3)^+$ yielding the corresponding isoprene derivatives $[Pd_2(\mu - PBu'_2)(\mu,\eta^2,\eta^2\text{-isoprene})(PR_3)_2]^+$, as BF₄ or triflate salts [5, 6]. The cooperation between the two metal centers in the coordination of the bidentate ligand was demonstrated also in these cases. The diene molecule, with the two double bonds in a *trans* configuration, was in fact shown to simultaneously coordinate to both metals of the $[Pd_2(\mu - PBu'_2)(PR_3)_2]^+$ fragment. The same type of reaction is given by the phosphite cations $(4a)^+$



(7a)⁺ : R = Me (7b)⁺ : R = Et and $(4b)^+$ (eq. 3). In fact, after the addition of a 10:1 molar excess of isoprene, a CDCl₃ solution of (4a)BF₄ (or (4b)BF₄) exhibited in the ${}^{31}P{}^{1}H{}$ NMR spectrum new resonances assigned to the diene derivatives $(7a)BF_4$ and $(7b)BF_4$, together with the resonances of the starting complexes, considerably broadened. Analogously to the reactions with CS₂ described above, the equilibrium (eq. 3) is greatly shifted to the left when the phosphite is $P(OMe)_3$ and to the right when the phosphite is $P(OEt)_3$. As shown earlier for the corresponding phosphine complexes, the spectrum of $(7a)^+$ (or $(7b)^+$) is due to an ABX spin system, where X is the bridging phosphorus and A and B are the similar, but unequivalent, phosphite P-nuclei (δ_A , $\delta_{\rm B}, \delta_{\rm X}$ and $J_{\rm AX} \approx J_{\rm BX}$ were respectively found at 134.2, 132.8, 381.9 ppm and 53 Hz for (7a)BF₄ and at 129.2, 127.4, 379.9 ppm and 51 Hz for (7b)BF₄).

Reactions with CO Carbon monoxide was bubbled into orange solutions of complexes (**4a**,**b**)BF₄. An immediate, hardly perceptible, bleaching of the solutions, together with the appearance of weak to medium v_{CO} absorptions around 2070 cm⁻¹ in the IR spectra, was observed. The ³¹P{¹H} NMR spectra of the solutions exhibited broad signals practically in the same positions of those due to the starting materials. These results can be explained by the substitution of a phosphite ligand by a CO molecule, giving [Pd₂(μ -PBu²₂)(CO){P(OR)₃}]BF₄[(**8a**)BF₄, R=Me; (**8b**)BF₄, R=Et], as shown in eq. 4. ligands have been prepared in good yields and purity. At least with the phosphites employed in this work, electronically unsaturated derivatives bearing only three phosphite ligands proved to be too unstable to be isolated or even observed as transient species. The corresponding derivatives bearing phosphine ligands were shown to be isolable when the bulkier phosphines [as in complex $(2)BF_4$] are employed, or when at least one of the phosphines is secondary, and can saturate the electronic deficiency of the tricoordinated palladium center by donating the electrons of the P-H bond [as in the phosphine-bridged (1)BF₄]. It was instead possible to isolate, although not pure, a stable derivative with three mixed phosphine-phosphite terminal ligands, complex (5)BF₄. This is probably stable due to the presence of a PPh₃ molecule, bulkier than $P(OPh)_3$, which was in fact found to be adjacent to the unsaturated palladium center.

The results observed by studying the reactivity of $(4a,b)BF_4$ parallel those reported previously for their phosphine analogues, in fact both react with CO, CS₂ and isoprene equilibrating, respectively, with the corresponding derivatives $(6-8a,b)BF_4$.

As expected, the reactivity of these systems is highly dependent upon the dimensions of the ligands, since equilibria involving the trimethyl phosphite derivative $(4a)BF_4$, compared to those involving the triethyl phosphite analogue $(4b)BF_4$, are much more shifted towards the reactants. Since solution NMR spectra



Equilibrium 4 should be far shifted to the left since the NMR resonances are not significantly shifted with respect to those of (**4a,b**)BF₄; their severe broadening is assignable either to the rate of the direct and forward reactions of eq. 4 or to exchange equilibria between coordinated and released P(OR)₃ molecules. An equilibrium analogous to that shown in eq. 4 was observed when studying the reaction of the trimethylphosphine derivative (**3a**)BF₄ with carbon monoxide, yielding $[Pd_2(\mu - PBu'_2)(CO)(PMe_3)_3]BF_4$, this equilibrium is completely shifted to the right under 1 Atm of CO, but is easily reverted by reducing P_{CO} [5].

CONCLUSIONS

The new complexes $(4a-c)BF_4$, with a central $Pd_2(\mu - PBu'_2)$ core binding four terminal phosphite

showed that the reactivity of the phosphite complexes towards CO, CS_2 and isoprene does not differ significantly from that of the phosphine derivatives we did not proceed further in the isolation of the products of these reactions.

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REFERENCES

 (a) Hayter, R. G. and Humiec, F. S., *Inorg. Chem.*, 1963, 2, 306. (b) Brandon, J. B. and Dixon, K. R., *Can. J. Chem.*, 1981, 59, 1188. (c) Arif, A. M., Heaton, D. E., Jones, R. A. and Nunn, C. M., *Inorg. Chem.*, 1987, **26**, 4228.

- (a) Sommovigo, M., Pasquali, M., Leoni, P., Braga, D. and Sabatino, P., *Chem. Ber.*, 1991, **124**, 97. (b) Leoni, P., Sommovigo, M., Pasquali, M., Sabatino, P. and Braga, D., *J. Organomet. Chem.*, 1992, **423**, 263.
- (a) Albinati, A., Lianza, F., Pasquali, M., Sommovigo, M., Leoni, P., Pregosin, P. S. and Ruegger, H., *Inorg. Chem.*, 1991, **30**, 4690. (b) Leoni, P., Pasquali, M., Sommovigo, M., Laschi, F., Zanello, P., Albinati, A., Lianza, F., Pregosin, P. S. and Rüegger, H., *Organometallics*, 1993, **12**, 1702.
- 4. (a) Leoni, P., Pasquali, M., Sommovigo, M., Albi-

nati, A., Lianza, F., Pregosin, P. S. and Rüegger, H., *Organometallics*, 1994, **13**, 4017. (b) Leoni, P., Pasquali, M., Pieri, G., Albinati, A., Pregosin, P. S. and Rüegger, H., *Organometallics*, 1995, **14**, 3143.

- Leoni, P., Pasquali, M., Sommovigo, M., Albinati, A., Pregosin, P. S. and Rüegger, H., Organometallics, 1996, 15, 2047.
- Leoni, P., Pasquali, M., Sommovigo, M., Albinati, A., Lianza, F., Pregosin, P. S. and Rüegger, H., Organometallics, 1993, 12, 4503.
- Leoni, P., Pasquali, M., Fadini, L., Albinati, A., Hofmann, P. and Metz, M., J. Am. Chem Soc., 1997, 119, 8625.
- 8. Leoni P. and Pasquali, M., unpublished results.