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Preliminary communication

Phosphido-bridged heterodinuclear complexes of CrPd, MoPd, WPd, and MnPd. X-Ray crystal structures of $[\text{Cp}(\text{CO})_2\text{Mo}(\mu\text{-PCy}_2)\text{Pd}(\text{PCy}_2\text{H})_2]$ and $[(\text{CO})_4\text{Mn}(\mu\text{-PCy}_2)\text{Pd}(\text{PCy}_2\text{H})_2]$

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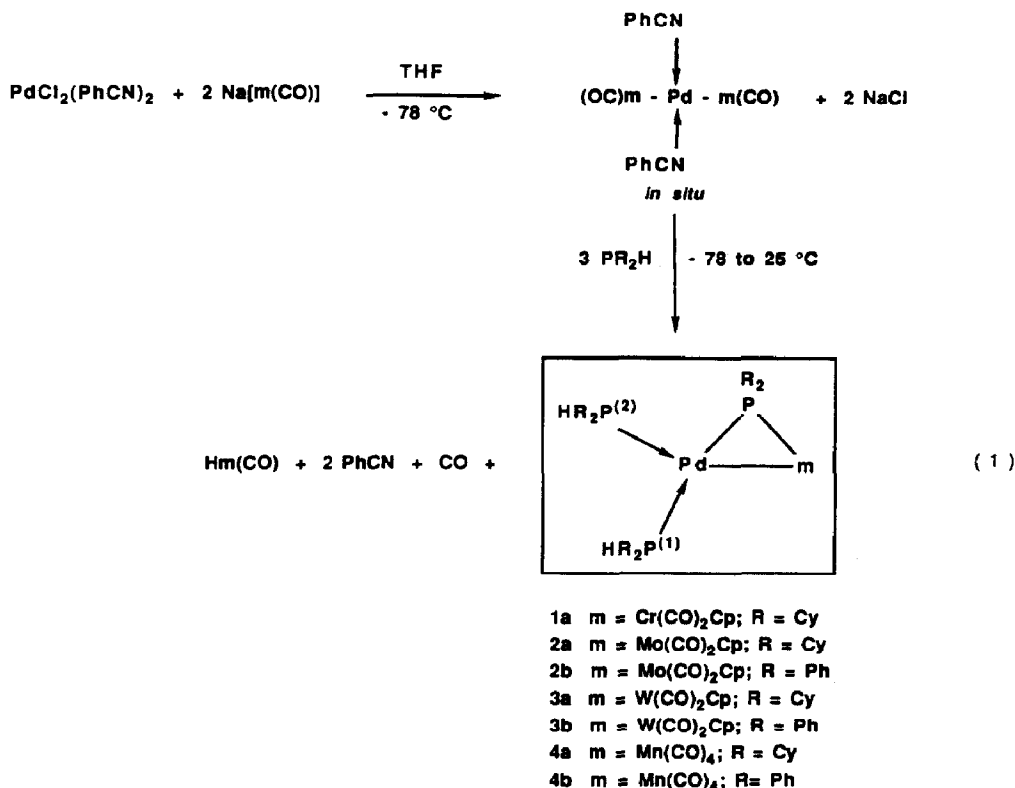
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Abstract

A series of phosphido-bridged heterodinuclear complexes has been prepared by the low temperature reaction of the labile chain complexes *trans*- $[\text{Pd}\{\text{m}(\text{CO})\}_2(\text{PhCN})_2]$ ($\text{m} = \text{Cr}, \text{Mo}, \text{W}(\text{CO})_2\text{Cp}; \text{Mn}(\text{CO})_4$) with 3 molar equivalents of PCy_2H or PPh_2H . The crystal structures of $[\text{Cp}(\text{CO})_2\text{Mo}(\mu\text{-PCy}_2)\text{Pd}(\text{PCy}_2\text{H})_2]$ and $[(\text{CO})_4\text{Mn}(\mu\text{-PCy}_2)\text{Pd}(\text{PCy}_2\text{H})_2]$ compounds were determined: Mo–Pd 2.916(2) Å and Mn–Pd 2.689(2) Å.

Interest in the chemistry of phosphido-bridged heterometallic complexes has steadily increased since the first report of such complexes [1]. We have recently shown that complexes containing electron-rich $\text{M}(\mu\text{-PR}_2)\text{Pt}$ units may be prepared by the reaction of trinuclear mixed-metal chain complexes of the type *trans*- $[\text{Pt}\{\text{M}(\text{CO})_3\text{Cp}\}_2(\text{PhCN})_2]$ ($\text{M} = \text{Mo}, \text{W}; \text{Cp} = \eta\text{-C}_5\text{H}_5$) with secondary phosphines PR_2H ($\text{R} = \text{Ph}, \text{Cy}; \text{Cy} = \text{c-C}_6\text{H}_{11}$) [2].

We sought to extend this method to the synthesis of heterobimetallic complexes in which a palladium-transition metal bond would be supported by a bridging phosphido ligand. The labile chain complexes *trans*- $[\text{Pd}\{\text{m}(\text{CO})\}_2(\text{PhCN})_2]$ [3] were treated in situ with 3 molar equivalents of PCy_2H or PPh_2H (eq. 1). The reactions proceed by nucleophilic displacement of the labile benzonitrile ligands, followed by oxidative-addition of the P–H bond across a heterometallic bond. The reactivity of PPh_2H is generally greater than that of PCy_2H .



The $^{31}\text{P}\{^1\text{H}\}$ NMR data for the new complexes are very informative [4 *]. Each complex shows a downfield resonance (doublet of doublets), assigned to the bridging phosphido ligand, and two resonances (doublet of doublets) from the terminal phosphine ligands. The magnitude of the $J(\text{PP})$ coupling constants clearly indicates a transoid $\text{P}(1)\text{-Pd-(}\mu\text{-P)}$ arrangement, whereas $\text{P}(2)$ is in a *cis* position with respect to these Pd-P bonds. The data also show that complexes 1–4 all have structures similar to those determined by X-ray diffraction ** for the MoPd (2a) and MnPd (4a) complexes (Fig. 1 and 2).

In both binuclear complexes two dicyclohexylphosphine ligands are terminally bonded to the Pd atom and a dicyclohexylphosphido ligand bridges the two metals. In respect of the metal–metal bonds, the Pd atom is in a distorted square planar arrangement (largest deviation from the least-squares plane formed by the Pd, the three P atoms and the other metal in 2a and 4a is 0.151(6) and 0.018(3) Å, respectively). Alternatively, the geometry about the Pd atom may be viewed as trigonal-planar, reminiscent of that of $\text{Pd}(\text{PR}_3)_2(\text{olefin})$ complexes and consistent with the isolobal analogy between $\text{R}_2\text{P-m}$ and $\text{CH}_2=\text{CH}_2$ [5,6]. The coordination geometries of the Mo and Mn atoms are as expected: in 2a the coordination around the Mo atom can be described as a distorted four-legged piano stool defined by the cyclopentadienyl ring and by two carbon atoms from terminal carbonyls, the Pd

* Reference numbers with asterisks indicate notes in the list of references.

** See page C7.

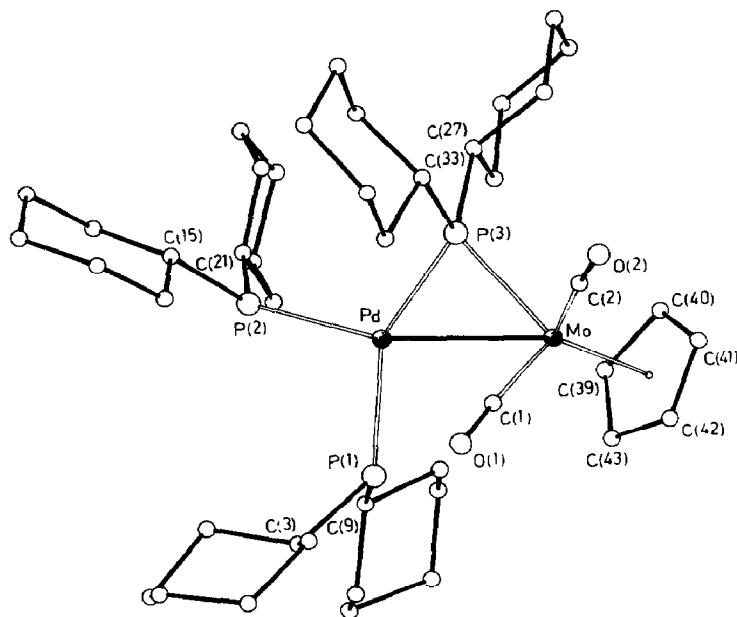


Fig. 1. View of the molecular structure of $(\eta\text{-C}_5\text{H}_5)(\text{CO})_2\text{Mo}(\mu\text{-PCy}_2)\text{Pd}(\text{PCy}_2\text{H})_2$ (**2a**). The H atom bound to P(1) and P(2) is not shown. Selected bond distances (Å) and angles ($^\circ$): Pd–Mo 2.916(2), Pd–P(1) 2.362(4), Pd–P(2) 2.380(5), Pd–P(3) 2.278(4), Mo–P(3) 2.367(3); Mo–Pd–P(1) 97.1(1), Mo–Pd–P(3) 52.5(1), P(1)–Pd–P(2) 96.7(2), P(2)–Pd–P(3) 113.7(2), Pd–P(3)–Mo 77.7(1).

** Crystal data for $\text{C}_{43}\text{H}_{73}\text{MoO}_2\text{P}_3\text{Pd}$ (**2a**): $M = 917.31$, triclinic, space group $P\bar{1}$, a 10.837(5), b 20.625(8), c 10.536(6) Å, α 92.34(2), β 107.34(2), γ 75.51(2) $^\circ$, V 2175(2) Å³, $Z = 2$, D_c 1.401 g cm⁻³, $F(000) = 960$, $\mu(\text{Mo-K}\alpha)$ 8.30 cm⁻¹, $\lambda(\text{Mo-K}\alpha)$ 0.71069 Å, intensities of 6866 independent reflections with θ in the range 3–24 $^\circ$ were measured on a Siemens AED diffractometer, $\theta/2\theta$ scan mode, dimensions of the crystal 0.24 × 0.32 × 0.40 mm. The structure was solved by Patterson and Fourier methods and refined by full-matrix least squares [15] first with isotropic and then with anisotropic thermal parameters for all the non hydrogen atoms using 3405 observed reflections [$I \geq 2\sigma(I)$]. The hydrogen atoms were placed at their geometrically calculated positions and included in the final structure factor calculation. Final R and R_w values are 0.061 and 0.67, respectively. Scattering factors were taken from ref. 16.

Crystal data for $\text{C}_{40}\text{H}_{68}\text{MnO}_4\text{P}_3\text{Pd}$ (**4a**): $M = 867.24$, monoclinic, space group $P2_1/n$, a 21.583(7), b 18.650(7), c 10.900(5) Å, β 96.36(2) $^\circ$, V 4361(3) Å³, $Z = 4$, D_c 1.321 g cm⁻³, $F(000) = 1824$, $\mu(\text{Mo-K}\alpha)$ 8.28 cm⁻¹, $\lambda(\text{Mo-K}\alpha)$ 0.71069 Å, intensities of 8104 independent reflections with θ in the range 3–25 $^\circ$ were measured on an Enraf–Nonius CAD4 diffractometer, $\omega/2\theta$ scan mode, dimensions of the crystal 0.20 × 0.25 × 0.28 mm. The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares [15] first with isotropic and then with anisotropic thermal parameters for all the non hydrogen atoms, excepting the cyclohexyl carbons, using 5266 observed reflections [$I \geq 3\sigma(I)$]. The hydrogen atoms were placed at their geometrically calculated positions and included in the final structure factor calculation. Final R and R_w values are 0.090 and 0.102 respectively. Scattering factors were taken from ref. 16. All calculations were performed on the CRAY X-MP/12 computer of the Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale, Bologna. Tables of atomic coordinates, a list of bond distances and angles, a list of thermal parameters and a list of observed and calculated structure factors for both compounds have been deposited with the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. They may be obtained on request from the Director by citing the full literature reference to this communication.

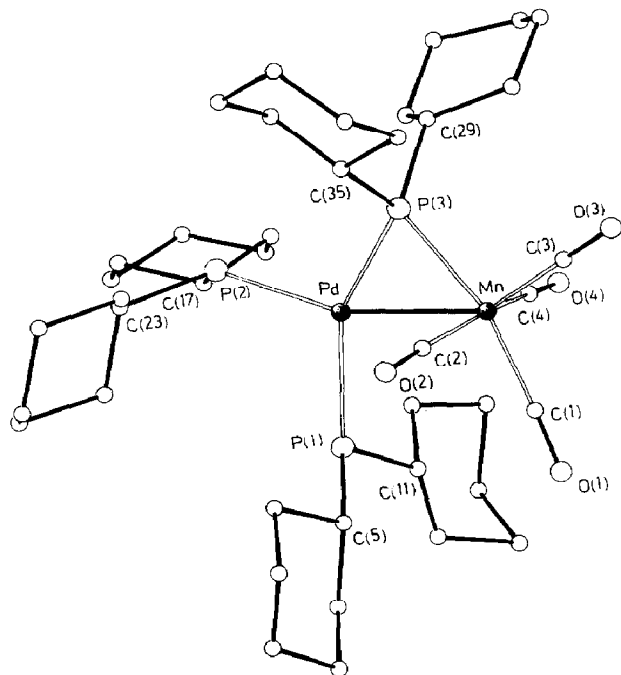
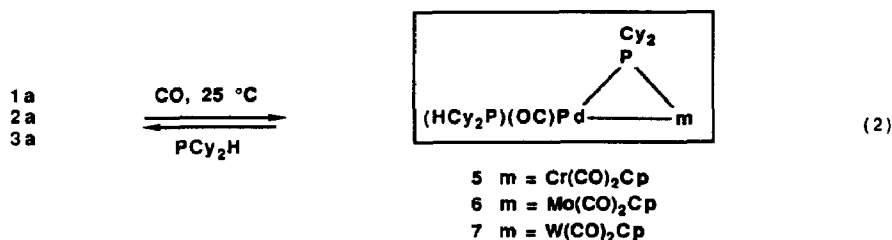


Fig. 2. View of the molecular structure of $[(\text{CO})_4\text{Mn}(\mu\text{-PCy}_2)\text{Pd}(\text{PCy}_2\text{H})_2]$ (**4a**). The H atom bound to P(1) and P(2) is not shown. Selected bond distances (Å) and angles ($^\circ$): Pd–Mn 2.689(2), Pd–P(1) 2.371(3), Pd–P(2) 2.312(3), Pd–P(3) 2.245(3), Mn–P(3) 2.263(3); Mn–Pd–P(1) 97.9(1), Mn–Pd–P(3) 53.7(1), P(1)–Pd–P(2) 100.9(1), P(2)–Pd–P(3) 107.5(1), Pd–P(3)–Mn 73.3(3).

atom and the P atom from the bridging PCy_2 ligand as legs. In **4a** the distorted octahedral coordination of the Mn atom is defined by four terminal carbonyl groups, the Pd atom and the P atom of the bridging PCy_2 ligand. A comparison of the two structures reveals an interesting feature. The Mo–Pd distance of 2.916(2) Å is one of the longest reported for such a bond, which has been found previously in the range 2.723(2) Å [7] – 3.059(1) Å [8], and is much longer than that in $[(\text{CO})_4\text{Mo}(\mu\text{-PCy}_2)_2\text{Pd}(\text{PPh}_3)]$, 2.760(1) Å, in which the two metals are connected by two PCy_2 bridges [9] or in $\text{MoPd}(\mu\text{-Ph}_2\text{py})_2(\mu\text{-CO})(\text{CO})_2$, 2.817(1) Å, which contains two 2-(diphenylphosphino)pyridine and one carbonyl bridges [10]. It is noteworthy that in $[(\text{CO})_4\text{Mo}(\mu\text{-PCy}_2)_2\text{Pd}(\text{PPh}_3)]$ the PCy_2 bridges are more asymmetrical than that in **2a**, the Mo–P distances being 2.530(1) and 2.542(2) Å and the Pd–P distances 2.287(2) and 2.267(2) Å [9]. The Mn–Pd separation of 2.689(2) Å is in the range reported for such metal–metal bonds, 2.580(2)–2.821(2) Å [11], but is shorter than that in the only other structurally characterized MnPd dinuclear complexes, $\text{MnPdX}(\text{CO})_3(\mu\text{-dppm})_2$ (X = Cl, 2.814 Å [12], X = Br, 2.810(2) Å [13]), in which the two metals are doubly bridged by dppm ligands.

The PCy_2H complexes **1a–3a** react partially with CO ($\text{CH}_2\text{Cl}_2/\text{C}_6\text{D}_6$, 25 $^\circ\text{C}$) with replacement of a terminal phosphine ligand, to give an equilibrium involving **5–7**, the liberated PCy_2H , and the excess of CO (eq. 2). Complexes **5–7** could be characterized in solution by IR and $^{31}\text{P}\{^1\text{H}\}$ NMR [14*] spectroscopy in contrast to their Mn–Pd analogue which is too reactive toward the free phosphine present in the solution. The lability of the Pd-bound ligands is also shown by the room temperature CO-catalyzed process that makes P(1) and P(2) atoms of the



latter complex equivalent in solution. This process is likely to involve transient CO coordination and phosphine dissociation. It can be shown by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy that complexes 5–7 are formed as *cis* and *trans* isomers with respect to the $\mu\text{-PR}_2$ ligand.

Even when the reaction of eq. 1 was performed with two molar equivalents of PR_2H , 1–3 were obtained as major products, although in lower yields, and only traces of 5–7 were observed by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy. This contrasts with the corresponding platinum chemistry [2]. Further comparison of the reactivities of these heterodinuclear complexes with those of their Pt analogues is in progress.

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- 4 Experimental methods and instruments were as given in ref. 2. All new compounds gave satisfactory elemental analyses and selected spectroscopic data are given below. ^1H NMR spectra were measured in C_6D_6 (ppm, ref. TMS int.), and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra in $\text{CH}_2\text{Cl}_2/\text{C}_6\text{D}_6$ (ppm, ref. H_3PO_4 ext.). $[\text{Cp}(\text{CO})_2\text{Cr}(\mu\text{-PCy}_2)\text{Pd}(\text{PCy}_2\text{H})_2]$ (1a). IR (CH_2Cl_2 , cm^{-1}) $\nu(\text{CO})$: 1861vs, 1786vs. ^1H NMR δ : 4.97 (s, 5H, C_5H_5), 4.37 (dm, 2H, PCy_2H). $^{31}\text{P}\{^1\text{H}\}$ NMR δ : 285.9 (dd, 1P, PCy_2 , $J(\text{PP})$ 121 and 39 Hz), 9.7 (d, 1P, P(1), $J(\text{PP})$ 121 Hz, from ^{31}P NMR: $J(\text{PH})$ 290 Hz), 7.0 (d, 1P, P(2), $J(\text{PP})$ 39 Hz, from ^{31}P NMR: $J(\text{PH})$ 293 Hz).
- $[\text{Cp}(\text{CO})_2\text{Mo}(\mu\text{-PCy}_2)\text{Pd}(\text{PCy}_2\text{H})_2]$ (2a). IR (CH_2Cl_2 , cm^{-1}) $\nu(\text{CO})$: 1878vs, 1790vs. ^1H NMR δ : 5.42 (s, 5H, C_5H_5), 4.33 (dm, 2H, PCy_2H). $^{31}\text{P}\{^1\text{H}\}$ NMR δ : 261.6 (dd, 1P, PCy_2 , $J(\text{PP})$ 153 and 23 Hz), 10.8 (dd, 1P, P(1), $J(\text{PP})$ 153 and 17 Hz, from ^{31}P NMR: $J(\text{PH})$ 292 Hz), 0.69 (pseudo t, 1P, P(2), from ^{31}P NMR: $J(\text{PH})$ 290 Hz).
- $[\text{Cp}(\text{CO})_2\text{W}(\mu\text{-PCy}_2)\text{Pd}(\text{PCy}_2\text{H})_2]$ (3a). IR (CH_2Cl_2 , cm^{-1}) $\nu(\text{CO})$: 1871vs, 1788 vs. ^1H NMR δ : 5.39 (s, 5H, C_5H_5), 4.27 (dm, 2H, PCy_2H). $^{31}\text{P}\{^1\text{H}\}$ NMR δ : 221.4 (dd with W satellites, 1P, PCy_2 , $J(\text{PP})$ 158 and 27 Hz, $J(\text{PW})$ 366 Hz), 6.75 (dd, 1P, P(1), $J(\text{PP})$ 158 and 13 Hz, from ^{31}P NMR: $J(\text{PH})$ 296 Hz), -11.9 (pseudo t, 1P, P(2), from ^{31}P NMR: $J(\text{PH})$ 278 Hz).
- $[(\text{CO})_4\text{Mn}(\mu\text{-PCy}_2)\text{Pd}(\text{PCy}_2\text{H})_2]$ (4a). IR (CH_2Cl_2 , cm^{-1}) $\nu(\text{CO})$: 1996m, 1904vs, 1888sh. ^1H NMR δ : 4.50 (dm, 1H, PCy_2H), 4.30 (dm, 1H, PCy_2H). $^{31}\text{P}\{^1\text{H}\}$ NMR δ : 228.3 (dd, 1P, PCy_2 , $J(\text{PP})$ 194 and 20 Hz), 14.3 (dd, 1P, P(1), $J(\text{PP})$ 194 and 30 Hz, from ^{31}P NMR: $J(\text{PH})$ 292 Hz), 3.8 (dd, 1P, P(2), $J(\text{PP})$ 30 and 20 Hz, from ^{31}P NMR: $J(\text{PH})$ 290 Hz).
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- 14 *Reactions with CO.* Solutions 5×10^{-2} M of compounds 1–4 in $\text{CH}_2\text{Cl}_2/\text{C}_6\text{D}_6$ (1/1) were prepared in 10 mm NMR tubes. CO was slowly bubbled through for 10 min and the tube sealed. For compounds 1a–3a, the solution contained ($^{31}\text{P}\{^1\text{H}\}$ NMR) an equilibrium mixture of these compounds, the *cis* and *trans* CO substituted 5–7 and free PCy_2H . Bubbling of N_2 through the solution resulted in CO elimination and complete regeneration of 1a–3a. For compounds 1b–3b and 4a, no substitution reaction was observed. For 4b no substitution was observable in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum at -70°C , but at 25°C the two phosphines became equivalent and no coupling was observed with the $\mu\text{-PPh}_2$ phosphorus atom. The coalescence temperature is -30°C .
 $[\text{Cp}(\text{CO})_2\text{Cr}(\mu\text{-PCy}_2)\text{Pd}(\text{CO})(\text{PCy}_2\text{H})]$ (5). $^{31}\text{P}\{^1\text{H}\}$ NMR δ : (*cis*, 77%) 294.0 (s, 1P, PCy_2), 2.4 (s, 1P, PCy_2H); (*trans*, 23%) 307.2 (d, 1P, PCy_2 , $J(\text{PP})$ 105 Hz), 10.0 (d, 1P, PCy_2H).
 $[\text{Cp}(\text{CO})_2\text{Mo}(\mu\text{-PCy}_2)\text{Pd}(\text{CO})(\text{PCy}_2\text{H})]$ (6). $^{31}\text{P}\{^1\text{H}\}$ NMR δ : (*cis*, 85%) 267.4 (d, 1P, PCy_2 , $J(\text{PP})$ 24 Hz), -1.7 (d, 1P, PCy_2H); (*trans*, 15%) 282.0 (d, 1P, PCy_2 , $J(\text{PP})$ 119 Hz), 11.7 (d, 1P, PCy_2H).
 $[\text{Cp}(\text{CO})_2\text{W}(\mu\text{-PCy}_2)\text{Pd}(\text{CO})(\text{PCy}_2\text{H})]$ (7). $^{31}\text{P}\{^1\text{H}\}$ NMR δ : (*cis*, 84%) 226.7 (d, 1P, PCy_2 , $J(\text{PP})$ 26 Hz, $J(\text{PW})$ 180 Hz), -11.8 (d, 1P, PCy_2H); (*trans*, 16%) 239.1 (d, 1P, PCy_2 , $J(\text{PP})$ 117 Hz), 8.1 (d, 1P, PCy_2H).
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