Stereochemistry and Mechanism of Nucleophilic Attack by Dialkylamines on (π-Allyl)palladium Complexes

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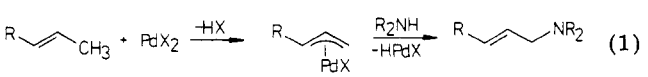
Nucleophilic attack by dialkylamines on the (π-allyl)palladium complex **1**, bis[(4-methoxy-1–3-η^3-cyclohexenyl)palladium chloride], in the presence of triphenylphosphine takes place exclusively with trans stereochemistry (>98% trans) to give *cis*-3-(dimethylamino)-6-methoxycyclohexene (**2**) (with Me_2NH) or *cis*-3-(diethylamino)-6-methoxycyclohexene (**3**) (with Et_2NH). In the presence of $AgBF_4$ and triphenylphosphine two additional products, *trans*-3-(diethylamino)-6-methoxycyclohexene (**4**) and 3-(diethylamino)-4-methoxycyclohexene (**5**), are formed (**4** up to 14% relative to **3**). Carbonylation of **1** in the presence of diethylamine gave the amide **6** regiospecifically, suggesting that a (σ-allyl)palladium complex is involved. NMR experiments suggest the formation of a σ-allyl complex on addition of phosphine ligands to **1**.

The introduction of an amine in the allylic position of an alkene is an important transformation in organic synthesis. So far there are no direct procedures known for this transformation, but methods leading to allylic amides have been reported.[1,2] In principle amination of (π-allyl)palladium complexes constitutes an allylic amination of an olefin since the π-allyl complex can be prepared directly from the olefin (eq 1). Dialkylamination of



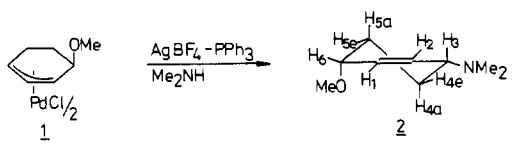
(1)

preformed (π-allyl)palladium complexes has been demonstrated,[3] and a preliminary stereochemical study indicates[4] that external trans attack by dialkylamine takes place. The stereochemical conclusion was based upon the fact that 3,6-bis(dimethylamino)cyclohexene was formed by palladium-assisted diamination of 1,3-cyclohexadiene, a result of trans aminopalladation of one of the double bonds followed by external trans attack on the intermediate (π-allyl)palladium complex.[4] Studies by Trost et al. suggest that a competing cis attack by amine also occurs.[5] Thus, palladium-catalyzed dialkylamination of *cis*- and *trans*-3-acetoxy-5-carbomethoxycyclohexenes in each case gave a cis–trans mixture of amine products. To account for these results, it was suggested[5] that about a third of the product arises from cis migration of the coordinated amine from palladium to carbon and the rest via external trans attack.

In view of extensive applications in organic synthesis of reactions involving nucleophilic attack on (π-allyl)palladium complexes,[6–9] further studies on the mechanism of these reactions seemed desirable. In this paper we have examined the stoichiometric dialkylamination of a (π-allyl)palladium complex and found that the major pathway is external trans attack by an amine nucleophile. Under certain conditions up to 14% cis addition takes place.

Results

The (π-allyl)palladium complex **1**, prepared by methoxypalladation of 1,3-cyclohexadiene (see Experimental Section), was used as a substrate for the mechanistic studies made here. We have previously established[10] the trans relationship between the methoxy group and the palladium atom in **1**, making this complex a suitable substrate for stereochemical studies. Treatment of **1** with equimolar amounts of $AgBF_4$ and PPh_3 in THF followed by addition of dimethylamine resulted in the precipitation of palladium black and formation of *cis*-3-(dimethylamino)-6-methoxycyclohexene (**2**) as the main product.



The cis configuration of **2** was established by ^1H NMR spectroscopy. The coupling constants $J_{3,4a}$ = 9.0 Hz and $J_{3,4e}$ = 5.4 Hz and $J_{5a,6} \approx J_{5e,6} \approx$ 3.5 Hz are only consistent with a cis configuration, with a preferred conformation in which the amino group is equatorial and the methoxy group is axial. The formation of the cis isomer **2** from **1** thus shows that the amine has attacked the π-allyl group from the face opposite to that of the metal (trans attack).

The analogous amination of **1** in THF using diethylamine also gave the *cis*-methoxy amine **3** as the major product by an external trans attack. However, careful analysis of the reaction mixture revealed the presence of two other isomeric products. Separation of these products

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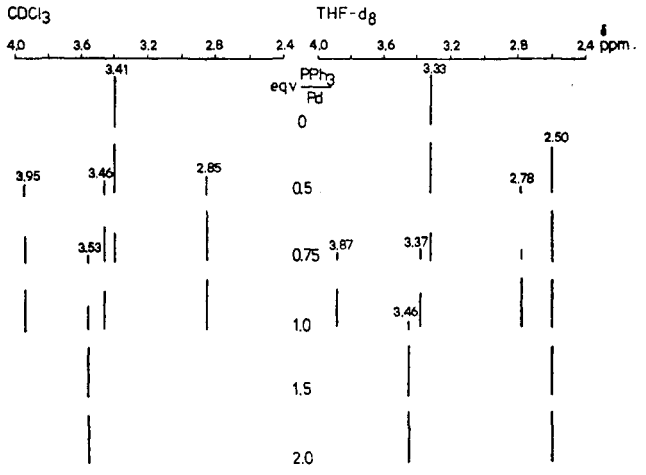
Table I. Nucleophilic Addition of Amines to 1

entry	PPh_3	$AgBF_4$	amine	solv	time, h	GC yield,[a] % 3	4	5	% cis addition product[b]
1	1		Et_2NH	THF	0.3	25	<0.5	<0.5	<2.0
					96	51	1.5	0.94	2.9
2	4		Et_2NH	THF	0.3	82	<1	0.8	<1.2
					1.5	82	3.0	0.9	3.7
					24	85	3.0	1.0	3.5
3	4		Me_2NH	THF	0.3	75	<1	~1	<1
					2	72	<1	~1	<1
					24	79	<1	~1	<1
					48	76	<1	~1	<1
4	4		Et_2NH	benzene	0.3	90	0.6	<0.5	0.6
					3.5	87	0.6	0.3	0.6
					20	82	0.5	<0.5	0.6
					216	83	0.6	<0.5	0.8
5	1	1	Et_2NH	THF	0.3	56	4.5	4.3	7.4
					2	76	6.2	3.6	7.5
					4	74	6.1	3.4	7.6
					24	87	8.1	4.2	8.5
6	4	1	Et_2NH	THF	0.3	66	6.7	3.2	9.2
					1	67	6.4	3.6	8.7
					4	67	6.4	3.8	8.7
					24	62	9.5	6.0	13
					120	24	24	19	50
7	4	1	Et_2NH	benzene	0.3	65	9.8	5.2	13
					3	62	9.6	5.5	13
					24	58	9.7	5.4	14
8	10	1	Et_2NH	THF	4.5	57	9.3	8.0	14

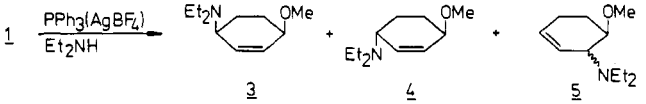
[a] The reactions were run in 1-mmol scale (see Experimental Section) and followed by GLC, using tetradecane as internal standard. Samples from the reaction were taken at different times. The samples were shaken with 2 M NaOH and ether before GLC analysis. [b] [4/(3 + 4)] × 100.

Table II. NMR Studies of 1 when Adding PPh_3 in $CDCl_3$ and THF-d_8[a]



[a] The height of the signals represents the intensity of the MeO resonances.

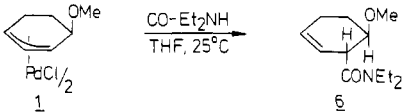
by preparative gas chromatography followed by NMR analysis showed that they were *trans*-3-(diethylamino)-6-methoxycyclohexene (**4**)[12a] and 3-(diethylamino)-4-methoxycyclohexene (**5**).[12b] The ratio between **3**, **4**, and **5**

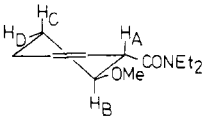


depends on the reaction conditions (Table I). Thus, the use of phosphines in the absence of $AgBF_4$ resulted in a highly regio- and stereospecific reaction (>98 % trans attack) to give essentially only **3**, whereas the presence of 1 equiv of $AgBF_4$ increased the amount of the cis addition product **4**. Interestingly, increasing the amount of phosphine in the presence of 1 equiv of $AgBF_4$ slightly increased the relative amount of **4**. Using benzene as the solvent gave a small but significant increase of products **4** and **5**. The results in Table I also show that some secondary isomerization takes place with time (entry 6).

In order to gain some knowledge about the nature of the reactive allylpalladium complexes (σ or π) involved in the amination reactions, experiments were performed with the aim to (i) trap the intermediate by carbonylation and (ii) observe the intermediate by NMR spectroscopy.

Reaction of **1** with diethylamine in the presence of carbon monoxide gave the amide **6** as the product with only traces of the amine products **3**–**5**. The other regioisomer, 1-((diethylamino)carbonyl)-4-methoxy-2-cyclohexene, also expected from carbon monoxide insertion, could not be detected. The trans configuration of **6** follows





J_{AB} = 7.7 Hz, J_{BC} = 10.8 Hz, J_{BD} = 3.1 Hz

from its ^1H NMR spectrum. Thus, the coupling constant J_{AB} = 7.7 Hz is in the range for a trans coupling. The other coupling constants J_{BC} and J_{BD} are consistent with the favored conformation with a trans relationship between the substituents.

(12) (a) The stereochemical assignment of the cis and trans isomers **3** and **4** was done by comparing the width at the half-height (W_H) of *CH*–OMe for the compounds. Thus, $(W_H)_{cis}$ = 8 Hz and $(W_H)_{trans}$ = 13 Hz. (b) We were not able to conclusively establish the stereochemistry of **5** from its NMR spectrum, since the chemical shift for the protons *CH*–O and *CH*–N is almost the same.

The reaction of 1 with triphenylphosphine was studied by ^1H NMR spectroscopy. The resulting mixture between 1 and the new complexes gave complicated NMR spectra, although it was easy to follow these equilibria by looking at the singlet of the methoxy group. Two solvents chloroform-*d* and tetrahydrofuran-d_8 were used and gave slightly different results. The most obvious change with either solvent after the addition of 0.5 equiv of triphenylphosphine is the appearance of a high-field methoxy resonance (δ 2.50 (THF-d_8) and 2.85 ($CDCl_3$)). Addition of more phosphine results in an increase of the high-field methoxy signal, which in $CDCl_3$ disappears on further addition of phosphine. After 2 equiv of triphenylphosphine are added, there is only one observable complex in $CDCl_3$ (δ_{MeO} 3.54), whereas in THF-d_8 there is an equilibrium between the two complexes (δ_{MeO} 2.50 and 3.46, respectively). The results from the addition of phosphine to 1 are summarized in Table II.

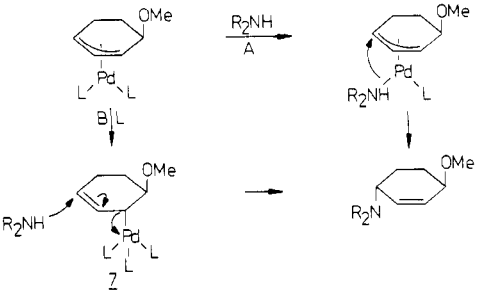
Discussion

The external trans attack observed here as the main path is in accordance with our previous observation[4] and with the fact that stabilized carbanions[13] and acetate[8a] in the presence of chloride ligands also add to (π-allyl)palladium complexes according to this mode. External trans attack is also observed for nucleophile addition to other transition-metal complexes having unsaturated hydrocarbon ligands.[14] However, hydride[15] and alkyl[16] are known to add to (π-allyl)palladium complexes from the same side as the metal (cis), and coordinated acetate has recently been shown[8a,10] to migrate from the metal to the π-allyl group in a cis addition process. The results obtained from palladium-catalyzed amination of allylic acetates[5] suggest the involvment of cis addition of amine in an intermediate (π-allyl)palladium complex, although trans addition dominates in this case in accordance with our own studies.[4]

The results from the stoichiometric dialkylamination of 1 in the presence of phosphines show that only trans attack (>98%) by the amine takes place when chloride is the counterion to palladium. Our experimental data in this case do not allow us to distinguish whether the traces of the cis addition product is a result of a cis migration pathway or a result of a secondary isomerization of the primary product 3. Such a cis–trans isomerization, as well as 1,4 to 1,2 isomerization was observed in some cases when the reaction mixture was left for a long time (entry 6). Furthermore, it is known that allylic amines can undergo positional isomerization in the presence of palladium(0) phosphine complexes.[17]

The formation of products 4 and 5 when BF_4^- is the counterion to palladium is not readily rationalized by a secondary isomerization, since the relative ratio between products 3, 4 and 5 was essentially the same after 0.3 and 4 h. It thus seems that a minor path via cis addition of amine is existing in the amination of 1 in the presence of $AgBF_4$ and triphenylphosphine. These results are in accord with observations by Trost et al.[5,7c] on the amination of allylic acetates using a homogeneous palladium(0) catalyst. For example, $Pd(PPh_3)_4$ catalyzed diethylamination of *trans*-3-acetoxy-5-carbomethoxycyclohexene in a ratio of 35:65. These results were explained by replacement of the acetoxy group by the metal with inversion to give a (π-allyl)palladium intermediate, followed by a competing cis and trans addition by amine, with the latter predominating. The use of a polymer-bound palladium catalyst gave a complete stereospecific reaction (trans attack by amine on the intermediate π-allyl complex). In our case the same effect giving a stereospecific reaction is obtained by using chloride ions as the counterion. The presence of chloride ions is known to direct nucleophilic addition of acetate to (π-allyl)palladium complexes and to go strictly with trans attack, a reaction which in the absence of chloride ions proceeds with cis attack in several cases.[8a]

Possible pathways for the formation of the cis addition product 4 are via cis migration of a coordinated amine (path A)[5,7c] or via formation of a (σ-allyl)palladium complex, 7, followed by a syn S_N2' attack by free amine (path B). The steric course of S_N2' displacements of various leaving groups by secondary amines is generally syn.[18] Now, if migration of amine from metal to carbon were the actual pathway for the cis addition product (path A), one would expect the cis attack to be depressed on addition to excess triphenylphosphine. Such an inhibition of cis migration of acetate from palladium to a coordinated allyl group has been observed on addition of chloride ions (as LiCl)[8a] or on addition of excess triphenylphosphine.[19]



We therefore ran three comparative experiments using 1, 4, and 10 equiv of triphenylphosphine in the amination of 1 in the presence of $AgBF_4$ (Table I, entries 5, 6, and 8). We do not observe any depression of cis addition when increasing the concentration of triphenylphosphine but observe a slight but significant[20] increase of the cis addition product. Thus, the ratio between the cis addition product 4 and the trans addition product 3 in the three experiments using 1, 4, and 10 equiv of PPh_3 were 1:12.1, 1:10.5, and 1:6.1, respectively. This corresponds to an increase of the relative amount of the cis addition product of 14 and 84% on going from 1 to 4 equiv of PPh_3 and from 1 to 10 equiv of PPh_3, respectively.[20] These results do not seem to fit a cis migration pathway (path A) but would fit an S_N2' pathway (path B). However, the present data do not allow us to differentiate between path A or path B. Furthermore it is also possible that cis migration can take place via a σ-allyl complex.[10]

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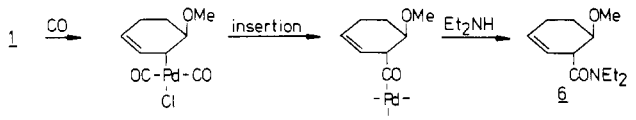
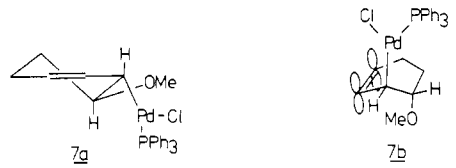
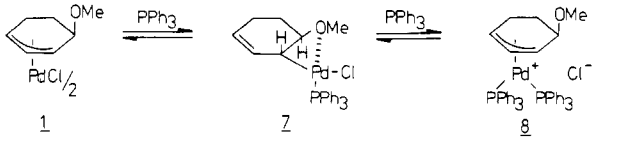
(20) We have repeated these experiments on the suggestion of one reviewer and found that the increase of cis addition on added triphenylphosphine is reproducible and that the difference is statistically meaningful. Thus the relative increase of the cis addition product 4 on going from 1 equiv of PPh_3 to 4 and 10 equiv of PPh_3 varied between 8 and 16% and 71 and 85%, respectively. The figures are based on three samples from each experiments taken at different times and each sample injected two or three times on GLC. The variations are within the expected errors from GLC determination.

The carbonylation of **1** to **6** is informative from a mechanistic point of view. First, it confirms that the methoxy group and palladium are trans also in a σ-allyl complex, since insertion of carbon monoxide into palladium–carbon bonds is known to occur with retention.[21] More importantly, it supports the formation of a σ-allyl complex on addition of ligands to **1**. It is remarkable that only the regioisomer **6** is formed and that none of the regioisomer from insertion into the other possible (σ-allyl)palladium bond is observed. This suggests that the (σ-allyl)palladium complex with palladium β to the methoxy group is strongly favored over the one with palladium δ to the methoxy group.



The dramatic change of the ^{1}H NMR spectrum of **1** on addition of triphenylphosphine deserves some comment. First, the appearance of the abnormally high-field methoxy resonance (δ 2.50 and 2.85 in THF-d_8 and $CDCl_3$, respectively) suggests a significant change of the conformation. With the assumption that σ-allyl complex **7** is formed, this would leave two possible explanations that account for the strong shielding of the methoxy group. In quasi-chair conformation **7a** with the substituents in equatorial positions, the methoxy group would appear in the shielding region of the metal. The other possibility is that a boat conformation is formed in which the methoxy group would be within the shielding region of the double-bond π system. The complex formed on further addition of phosphine (2 equiv) has the methoxy resonance at approximately 0.1 ppm lower field than in the parent complex **1**. In $CDCl_3$ this final complex (δ_{OMe} 3.54) is the sole complex after the addition of 2 equiv of phosphine, whereas in THF-d_8 there is an equilibrium between this complex (δ_{OMe} 3.46) and the one assigned as **7**. A likely structures for the new complex formed after addition of 2 equiv of phosphine is **8**.





The indication by ^{1}H NMR spectroscopy for the formation of σ-allyl complex **7** is consistent with the observation that carbonylation of **1** gives **6**. It is therefore possible that the cis addition product observed arises from an S_N2' attack (syn) by amine on a (σ-allyl)palladium complex such as **7**.

Concluding Remarks

The stereochemical studies in this work show that dialkylamines add to (π-allyl)palladium complexes via a stereospecific trans attack. When chloride is the counterion to palladium, the stereospecificity exceeds 98%. Although only one diastereoisomer of (4-methoxy-1-3-η^3-cyclohexenyl)palladium chloride was studied (the trans isomer), the result should be reliable, since the thermodynamically less stable cis isomer **3** is formed as the single product. When BF_4^- is the counterion, small amounts of the cis addition product are also observed (7–14% relative to the trans addition product). This product may be formed either via a cis migration pathway[5,7c] or via an S_N2' attack on a σ-allyl complex. We conclude that for (π-allyl)palladium complexes, external trans attack by amine is a more favored process than cis migration, in analogy to nucleophilic addition of amine to (π-olefin)-[22] and (σ-alkyl)palladium[23] complexes. However, the activation energies for cis and trans amination of (π-allyl)palladium complexes appear not to be far apart as originally suggested by Trost.[5,7c,24]

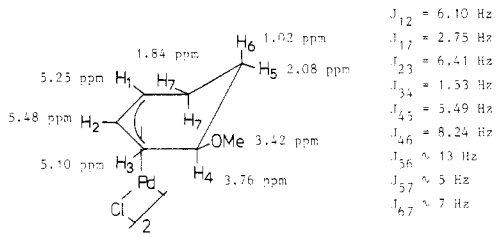


Figure 1. Bis[(4-methoxy-1-3-η^3-cyclohexenyl)palladium chloride], **1**: ^{1}H NMR ($CDCl_3$) data (δ relative to tetramethylsilane).

Experimental Section

Infrared spectra were recorded on a Perkin-Elmer 257 spectrophotometer. NMR spectra were obtained at 200 MHz with a Bruker WP 200 FT spectrometer. The mass spectra were determined with an LKB 9000 spectrometer. GLC analyses were run on a column packed with 10% Apiezon L and 10% KOH on Chromosorb W (60/80 mesh). Tetrahydrofuran (THF) was distilled from potassium/benzophenone under nitrogen. Benzene was distilled and stored over potassium hydroxide. Carbon monoxide was purchased from KEBO AB.

Preparation of Bis[(4-methoxy-1-3-η^3-cyclohexenyl)palladium chloride] (1). Complex **1** was prepared by a modified method of Robinson and Shaw.[25] To a cold (0 °C) stirred solution under nitrogen atmosphere of $Na_2PdCl_4 \cdot 3H_2O$ (1.0 g, 2.9 mmol) in methanol (5 mL) was added cyclohexadiene (0.5 mL, 5.2 mmol). Sodium chloride precipitated immediately. After 20 min the suspension was stored at −20 °C (freezer) for 15 h. The mixture was then filtred and washed with cold water and cold methanol and dried (desiccator 0.5 torr), yielding 0.65 g (90%) of **1** as a pale yellow powder. See Figure 1 for the NMR spectrum. It is important to keep the temperature at 0 °C during the reaction since stirring the solution at room temperature for 20 min gave a mixture of **1** and up to 10% of bis[(η^3-cyclohexenyl)palladium chloride].

General Procedure for Dialkylamination of 1. To a stirred solution of **1** (253 mg, 1.00 mmol of palladium) in THF (5 mL) under nitrogen at room temperature was added a solution of triphenylphosphine (1.05 g 4.0 mmol) in THF (2 mL). After 5 min diethylamine (0.73 mL, 7 mmol) was added. After the solution was stirred, for 3 h, 1 mL of 2 M NaOH was added and the aqueous phase extracted with ether (2 × 10 mL). The combined organic layer was filtered and extracted with 1 M HCl (3 × 7 mL). The acidic aqueous phase was washed with 7 mL of ether, made alkaline with solid KOH, and extracted with ether (3 × 7 mL). The organic phase was then washed with 7 mL of aqueous saturated NaCl, dried (K_2CO_3), filtered, and concentrated, yielding 143 mg (78%) of **3** as an oil: NMR ($CDCl_3$) δ 6.0–5.8 (m, 2, CH=CH), 3.60 (m, 1, CHO), 3.35 (s, 3, OMe), 3.33 (m (low-field peaks concealed), 1, CHN), 2.58 (q, 2, NCH_2), 2.48 (q, 2, NCH_2), 1.7–1.5 (m, 4, CH_2CH_2), 1.05 (t, J = 7.5 Hz, 6, CCH_3); IR (KBr)

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2962, 2930, 2870, 2920, 1095, 1080, 1070 cm^{-1}. Anal. Calcd for $C_{11}H_{21}NO$: C, 72.08; H, 11.55; N, 7.64. Found: C, 71.93; H, 11.69; N, 7.68.

The amination in the presence of $AgBF_4$ was done by using the same procedure as described above. In this case $AgBF_4$ (195 mg, 1 mmol) in THF (1 mL) was added immediately after the addition of triphenylphosphine. The isomeric amines **3**, **4**, and **5** were separated by preparative GLC. In the amination with dimethylamine the amine was added by using a 2.5 M solution in THF.

Spectral Data for Amines 2, 4, and 5. **2**: NMR ($CDCl_3$) δ 6.0–5.8 (m, 2, CH=CH), 3.64 (m, 1, CHO), 3.36 (s, 3, OMe), 3.09 (m, 1, CHN), 2.30 (s, 6, NMe_2), 1.7–1.5 (m, 4, CH_2CH_2).

4: NMR ($CDCl_3$) δ 5.85 (m, 1, =CH), 5.75 (m, 1, =CH), 3.84 (m, 1, CHO), 3.46 (m, 1, CHN), 3.36 (s, 3, OMe), 2.53 (q, 2, NCH_2), 2.45 (q, 2, NCH_2), 1.8–1.4 (m, 4, CH_2CH_2), 1.05 (t, J = 7.5 Hz, 6, CCH_3).

5: NMR ($CDCl_3$) δ 5.78 (m, 1, =CH), 5.54 (m, 1, =CH), 3.43 (s, 3, MeO), 3.34 (m, 2, CHO and CHN), 2.60 (q, 4, NCH_2), 2.1–1.9 (m, 4, CH_2CH_2), 1.06 (t, J = 7.3 Hz, 3, CCH_3).

Carbonylation of 1 in the Presence of Diethylamine. To a stirred solution of **1** (50 mg, 0.2 mmol of palladium) in THF at room temperature was added diethylamine (156 μL, 1,5 mmol) followed by bubbling carbon monoxide through the solution. After a few minutes palladium zero precipitated. After 3 h the conversion was complete (by GLC) and 0.5 mL of 2 M NaOH and 2 mL of ether were added. After filtration, the organic layer was separated and the aqueous phase was extracted with ether. The combined organic phase was washed with saturated NaCl(aq) and dried ($MgSO_4$). Evaporation of the solvent gave 20 mg of crude amide **6**. The product was purified by preparative TLC (silica gel, EtOAc/hexane, 1:1): R_f(TLC) 0.3; yield 20%; NMR ($CDCl_3$) δ 5.79 (m, 1, =CH), 5.34 (m, 1, =CH), 3.78 (ddd, J = 10.8, 7.7, and 3.1 Hz, 1, CHO), 3.6–3.3 (m, 5, NCH_2 and CHCO), 3.36 (s, 3, MeO), 2.3–2.1 (m, 2, CH_2), 1.7–1.4 (m, 2, CH_2) 1.22 (t, J = 7.1 Hz, 3, CCH_3), 1.13 (t, J = 7.1 Hz, 3, CCH_3); mass spectrum, m/e (relative intensity), 211 (M^+, 8), 196 (14), 107 (15), 100 (100), 81 (22), 78 (31), 77 (16), 72 (84), 53 (18), 44 (26).

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Synthesis and X-ray Crystal Structures of $[M(\mu\text{-}(t\text{-Bu})(H)P)(PMe_3)_2]_2$ (M = Rh, Ni) Containing Rh=Rh Double and Ni–Ni Single Bonds

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The isostructural, dinuclear complexes $[M(\mu\text{-}(t\text{-Bu})(H)P)(PMe_3)_2]_2$, M = Rh (**1**) and Ni (**2**), have been synthesized and characterized and their structures determined by X-ray diffraction studies. **1** can be isolated from the reaction of $[Rh(COD)Cl]_2$ with Li_2P-*t*-Bu in THF after treatment with excess PMe_3. **2** is formed from the reaction of $NiCl_2(PMe_3)_2$ and Li_2P-*t*-Bu in THF. The X-ray structures of **1** and **2** show two metal atoms, each bonded to two terminal PMe_3 ligands and bridged by two *tert*-butylphosphido ((*t*-Bu)(H)P^-) groups. The metal–metal distances and electron counts indicate the presence of double and single metal–metal bonds in **1** and **2**, respectively (Rh–Rh = 2.552 (2) Å and Ni–Ni = 2.559 (2) Å). The coordination geometry about each metal is distorted tetrahedral (ignoring the metal–metal interaction). Crystal data for **1**: monoclinic, space group $C2/m$ (No. 12), a = 17.495 (11) Å, b = 11.913 (2) Å, c = 8.815 (3) Å, β = 115.11 (4)°, U = 1664 (3) Å^3, Z = 2, D_{calcd} = 1.37 g cm^{-3}, λ(Mo Kα) (graphite monochromator) = 0.710 69 Å, μ(Mo Kα) = 11.60 cm^{-1}, T = 298 K. Refinement with 792 observed (1729 measured) reflections gave a final R = 0.044 and R_w = 0.049. Crystal data for **2**: monoclinic, space group $C2/m$ (No. 12), a = 17.871 (8) Å, b = 11.643 (7) Å, c = 8.833 (4) Å, β = 116.44 (3)°, U = 1646 (3) Å^3, Z = 2, D_{calcd} = 1.21 g cm^{-3}, λ(Mo Kα) (graphite monochromator) = 0.710 69 Å, μ(Mo Kα) = 14.44 cm^{-1}, T = 298 K. Refinement with 1059 observed (1158 measured) reflections gave R_1 = 0.0605 and R_w = 0.0655.

Introduction

There is growing interest in the chemistry of phosphido (R_2P^-) complexes of transition metals since these types of ligands can act as versatile bridging units between two or more metal centers. We have initiated a broad program aimed at the study of steric and electronic effects involved in these types of compounds. Our initial studies have focused on the use of the bulky di-*tert*-butylphosphido ($t\text{-}Bu_2P^-$) group.[1-5] We report here the synthesis and structures of two isostructural complexes of Rh(I) and Ni(I) in which the two metal atoms are bridged by the sterically less demanding *tert*-butylphosphido ((*t*-Bu)(H)P^-) group.

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