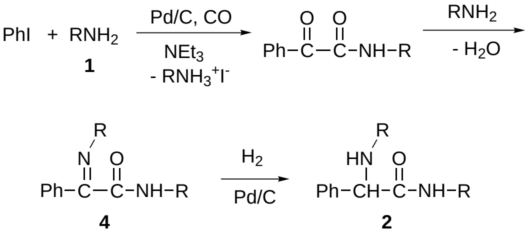
A possible pathway for the formation of α-amino amides (Scheme 1) may involve the following sequence: double carbonylation of the iodoarene to give the α-keto amide, amine condensation with the α-keto group of the latter to form an α-imino amide **4** as an intermediate, and hydrogenation of the imino double bond of **4** to give the α-amino amide **2**. α-Keto amide formation in the double carbonylation process can be considered to be related to that described by Yamamoto and co-workers, via formation of an acylcarbamoylpalladium intermediate followed by reductive elimination.[12] Palladium-catalyzed double carbonylation of aryl halides in the presence of a secondary amine to give α-keto amides has been extensively studied.[13] Using a primary instead of a secondary amine in the double carbonylation reaction has only been described in several papers.[5b, 12] However, the double carbohydroamination reaction sequence, described herein can, for the first time, produce α-amino amides in a one-pot manner. The formation of the amide by-product results by monocarbonylation of iodobenzene. The formation of the by-product imine can be attributed to competitive reactions of hydroformylation of iodobenzene with subsequent amine condensation.



Scheme 1. Reaction pathway for the double carbohyroamination of iodobenzene. **a**: R = cyclohexyl, **b**: R = *n*-butyl, **c**: R = benzyl.

In conclusion, palladium-catalyzed double carbohydroamination, consisting of double carbonylation, amine condensation, and hydrogenation, is a novel domino reaction for the one-pot production of α-amino amides. The reaction is simple in execution and workup, and is of considerable potential for the synthesis of α-amino amides and other α-amino acid derivatives.

Experimental Section

General procedure for the double carbohydroamination: A mixture of iodobenzene (0.112 mL, 1 mmol), cyclohexylamine (1.14 mL, 10 mmol), triethylamine (3 mL), Pd/C (10 %, 0.0213 g, 0.02 mmol), and 4Å molecular sieves (1 g) was placed in a 45-mL stainless steel autoclave equipped with a glass liner and magnetic stirrer. The autoclave was purged three times with carbon monoxide and then pressurized with CO and H_2, respectively, to the desired level (see Tables 1 and 2). The reaction was carried out in an oil bath for 24 h and the autoclave was cooled to room temperature and the gas was released. The reaction mixture was filtered through Celite, washed several times with CH_2Cl_2, and filtrate was evaporated to give a pale yellow oily residue. Addition of ether gave a white precipitate, identified as $CyNH_3^+I^-$. After filtration, the diethyl ether solution was evaporated and the resulting oil was subjected to ^{1}H NMR spectroscopy, and then to preparative TLC, using hexane/ethyl acetate as eluant, affording the pure α-amino amide.[10]

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[11] It is noteworthy that using a catalyst other than Pd/C, such as the palladium(0) complex $[Pd(PPh_3)_4]$ or palladium(II) complex $[PdCl_2(MeCN)_2]$, together with Ph_2MeP, gave rise to the formation of **4a** and oxamide CyNHCOCONHCy as major products, respectively.

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A Neutral Three-Coordinate Alkylrhodium(I) Complex: Stabilization of a 14-Electron Species by γ-C–H Agostic Interactions with a Saturated Hydrocarbon Group[**]

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Selective activation and functionalization of alkanes by transition metals is a highly attractive goal[1] which has led to considerable efforts to understand hydrocarbon interactions

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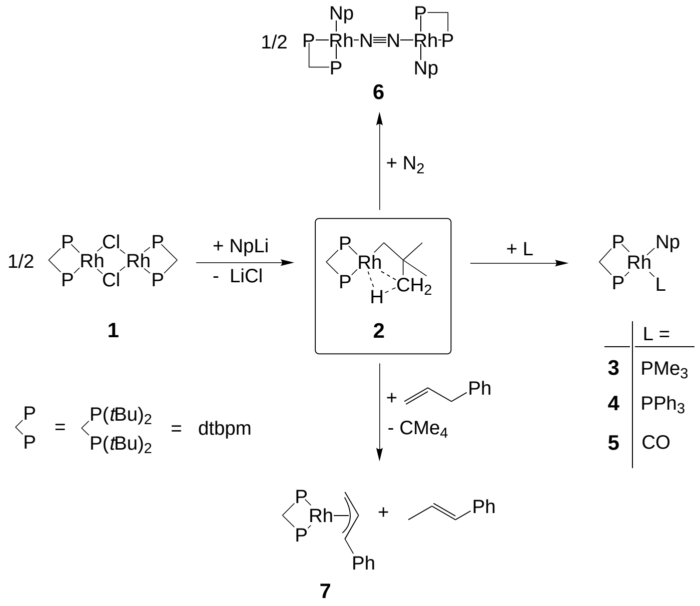
with vacant sites of transition metal centers. Three-coordinate, T-shaped, 14-electron d^8-ML$_3$ complexes play a vital role as key intermediates in many stoichiometric and catalytic transformations,[2] as exemplified by [RhCl(PPh$_3$)$_2$] from Wilkinson's catalyst and its congeners.[2a,3] Usually they are transient species generated in situ by ligand dissociation[4] or by hapticity changes of, for example, η^3-benzylic systems [L$_2$M(η^3-CH$_2$Ph)] (M = Rh, Ir).[2b,5] Stabilization of 14-electron d^8-ML$_3$ species has been achieved by using bulky *trans* ligands in *trans*-[RhX(PR$_3$)$_2$] complexes (X = H, Hal, σ-carboranyl; R = *t*Bu, *i*Pr, Cy, Ph), but their monomeric nature is either only postulated or deduced from molecular weight measurements in solution.[6,7] To date, only [Rh(PPh$_3$)$_3$]$^+$, [Ni(Mes)$_3$]$^-$ (Mes = 2,4,6-(CH$_3$)$_3$C$_6$H$_2$), and the olefin complexes [(LN$_2$)Rh(η^2-ene)] (LN$_2$ = β-diiminate; ene = cyclooctene, norbornene) have been structurally characterized.[8]

Here we report the synthesis, structure, and reactivity of the first neutral, three-coordinate alkylrhodium(I) complex [(κ^2-dtbpm)RhNp] (**2**), which contains the *cis*-chelating bis(di-*tert*-butylphosphanyl)methane[9] ligand (*t*Bu$_2$PCH$_2$P*t*Bu$_2$, dtbpm) and a neopentyl (Np) group (Scheme 1). The 14-electron Rh$^\text{I}$ center is weakly stabilized by agostic interactions with the γ-C–H bonds and possibly the β-C–C bond of the alkyl ligand. Owing to the availability of an "open" coordination site, **2** is an ideal model of uncharged three-coordinate d^8-[L$_2$Rh(alkyl)] transients and of isoelectronic, d^8-[L$_2$M(alkyl)]$^+$ ions (M = Ni$^{\text{II}}$, Pd$^{\text{II}}$), intermediates in late transition metal catalyzed olefin polymerization.[10]



Scheme 1. Synthesis and some reactions of **2**.

Treatment of [{(κ^2-dtbpm)RhCl}$_2$] (**1**)[6] with an excess of NpLi in a pentane suspension at $-20\,^\circ$C led to air- and moisture-sensitive **2** in 61 % yield.[11] The orange-red compound is moderately stable at 25 °C as a solid, but solutions of **2** have to be handled at lower temperatures, as rapid, unselective decomposition is observed above 0 °C. A single-crystal X-ray diffraction analysis of **2** revealed the expected planar T-shaped RhP$_2$C skeleton (Figure 1).[12]

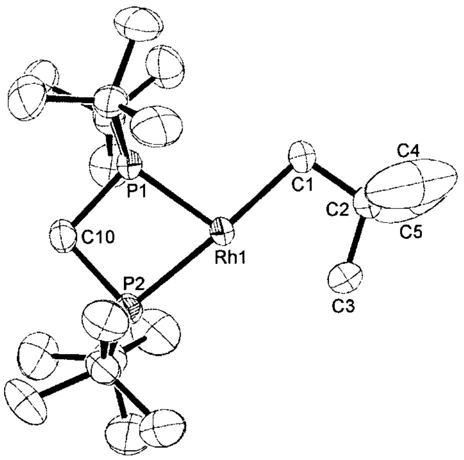


Figure 1. Molecular structure of **2** (ORTEP plot, 50 % probability ellipsoids, hydrogen atoms omitted for clarity). Selected bond lengths [Å] and angles [°]: Rh1-P1 2.172(1), Rh1-P2 2.314(1), Rh1-C1 2.082(4), Rh1-C2 2.804, Rh1-C3 2.491(4), C1-C2 1.521(5), C2-C3 1.498(5), C2-C4 1.443(6), C2-C5 1.463(6); P1-Rh1-P2 75.98(4), C1-Rh1-P1 101.01(11), C1-Rh-P2 176.60(14), Rh1-C1-C2 101.0(2), C1-C2-C3 109.0(3). Estimated Rh–H3 (assuming standard C–H bond lengths and angles): 1.55 (one H at C3 agostic) or 2.23 (for wedge position of two agostic hydrogen atoms).

The unsymmetric chelate ring Rh1-P1-C10-P2 and atoms C1, C2, and C3 of the neopentyl group are almost coplanar. The long Rh1–P2 bond (2.314(1) Å) is a consequence of the strong *trans* influence of the alkyl ligand, which is also reflected in the small Rh–P2 coupling constant[13] ^1J(P,Rh) of 99 Hz for P2 (dd, $\delta = 21.6$). The short Rh1–P1 bond of 2.172(1) Å and the correspondingly large ^1J(P,Rh) coupling constant of 280 Hz for the resonance of P1 (dd, $\delta = 54.2$) indicate a nearly negligible *trans* influence of the agostic hydrocarbon moiety.

The nature of this agostic interaction in **2** was studied by low-temperature ^{1}H NMR spectroscopy in [D$_8$]THF and [D$_8$]toluene.[11] All three methyl groups of the neopentyl ligand remain equivalent on the ^{1}H NMR time scale down to $-105\,^\circ$C, implying a very small rotational barrier for the neopentyl *t*Bu group. The methyl *doublet* resonance (^2J(H,P) = 2.2 Hz, assigned by ^{1}H and ^{1}H{^{31}P} NMR spectra) at $\delta = 0.83$ ($-30\,^\circ$C, [D$_8$]THF) confirms time-averaged γ-agostic interactions of all nine C–H bonds with the rhodium center.[14] It is impossible to establish the weak γ-C–H to Rh σ-complexation through C–H bond elongation in the solid-state structure, because the neopentyl methyl hydrogen atoms could not be localized. The very short[15] nonbonded Rh1–C3 distance of 2.491(4) Å and the small Rh1-C1-C2 angle (101.0(2)°), however, clearly reveal an attractive relationship of the metal center with one or two γ-C–H bonds and possibly with the C2–C3 bond in the β-position. In fact, this bond undergoes clean β-methyl elimination in the isoelectronic platinum cation [(κ^2-dtbpm)PtNp]$^+$, leading to isobutene and a metal-bound methyl group.[16] Thus, rhodium compound **2** might resemble a structure on the pathway of β-carbon elimination at d^8-ML$_2$ templates.[17]

Owing to the averaging out of all nine methyl protons of the Np group by *t*Bu and Me rotations, lowered C–H streching frequencies, upfield NMR shifts, or reduced ^{13}C–^{1}H coupling constants for the agostic hydrogen atoms are not observed for

2.[15] However, agostic interactions are unequivocally established for the solid-state structure and by all NMR data of **2** in solution.

The inequivalence of the two P nuclei at ambient temperature proves that barrier for T-Y-T inversion at the rhodium center lies well above 20 kcal mol^{-1}, consistent with theoretical predictions.[6, 18]

Agostic interactions in **2** were probed by density functional theory (DFT) calculations[19] on the model system [(κ^2-dhpm)RhNp] (**2a**; dhpm = bis(diphosphanyl)methane, $H_2PCH_2PH_2$). Its optimized geometry (Figure 2) is in good agreement with the solid-state structure of **2** and clearly displays an agostic C–H bond to the vacant coordination site.

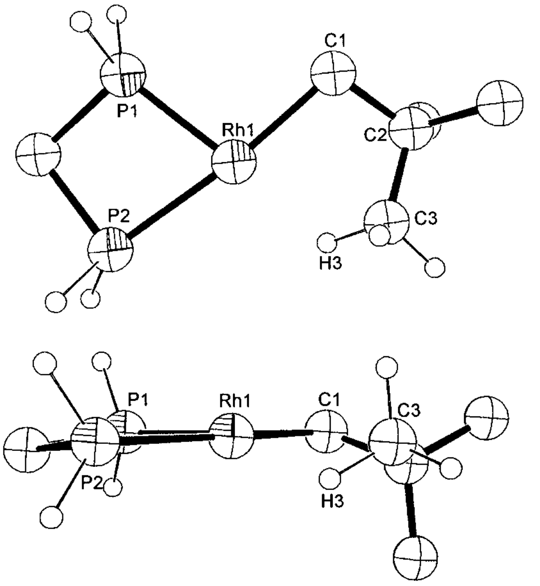


Figure 2. Optimized geometry of the model complex **2a** (DFT; some hydrogen atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: Rh1-P1 2.190, Rh1-P2 2.360, Rh1-C1 2.057, Rh1-C2 2.795, Rh1-C3 2.521, Rh1-H3 1.997, C1-C2 1.541, C2-C3 1.546, C3-H3 1.128; P1-Rh1-P2 74.2, C1-Rh1-P1 99.2, C1-Rh1-P2 173.4, Rh1-C1-C2 101.0, C1-C2-C3 105.2.

The metal-coordinated C3–H3 bond is elongated (1.128 Å compared to an average of 1.097 Å for the noncoordinated C–H bonds), and the short Rh–H3 distance (1.997 Å) indicates a moderaty strong interaction, which is also reflected in the computed low C3–H3 vibrational frequency of 2723 cm^{-1} and the short (2.190 Å) Rh–P1 distance (as opposed to Rh–P2, 2.360 Å), which establishes the weak donor character of the agostic C–H bond. The NMR equivalence of the nine methyl protons of **2** corresponds to tiny calculated barriers to rotation for the methyl (0.5 kcal mol^{-1}) and *t*Bu groups (2 kcal mol^{-1}) for **2a**. Neopentyl rotation occurs through a three-coordinate T-shaped transition state (8.6 kcal mol^{-1}) without σ complexation of C–H bonds.

In NMR experiments, ligands L (L = PMe_3, PPh_3, CO) instantaneously react with **2**, yielding square-planar complexes [(κ^2-dtbpm)RhNpL] **3**–**5** (Scheme 1). Compounds **3** and **5** were synthesized independently from NpLi, [(κ^2-dtbpm)RhCl(PMe_3)],[6] and [(κ^2-dtbpm)RhCl(CO)].[6] Their structures were established by X-ray diffraction.[12b,c] Unlike **3** and **5**, **4** dissociates in solution, forming **2** and PPh_3.

Treatment of a solution of **2** in pentane with 1 bar of N_2 led to the precipitation of the air- and moisture-sensitive dinuclear, dinitrogen-bridged complex [{(κ^2-dtbpm)RhNp}$_2$(μ-η^1:η^1-N_2)] (**6**) (Figure 3).[12b] To our knowledge, **6** represents the first dinuclear, doubly end-on dinitrogen-bridged, late transition metal complex with a *cis*-chelating diphosphane ligand.[20] Orange, sparingly soluble **6** is stable as a solid at ambient temperature, but loses N_2 in vacuo, undergoing undefined decomposition. In solution, N_2 loss above −10 °C regenerates **2**.

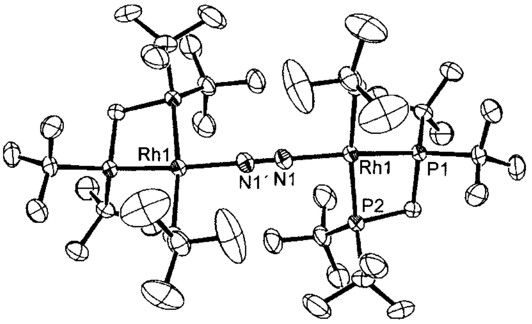


Figure 3. Molecular structure of **6** (ORTEP plot, 50% probability ellipsoids, hydrogen atoms omitted for clarity). Selected bond lengths [Å] and angles [°]: Rh1-P1 2.258(1), Rh1-P2 2.322(1), Rh1-C1 2.133(4), Rh1-N1 1.973(3), N1-N1′ 1.106(6); P1-Rh1-P2 75.35(4), N1-Rh1-C1 92.36(15), N1-Rh1-P1 166.42(9), N1-Rh-P2 95.99(10), N1′-N1-Rh1 169.56(9).

The alkylrhodium complex **2** also coordinates olefins and activates C–H bonds under mild conditions. The NMR spectrum recorded for the reaction of a solution of **2** in [D$_8$]THF with an excess of allylbenzene at −70 °C indicates the formation of two transient species. On raising the temperature, these transient species undergo benzylic C–H activation and neopentane elimination. The stable allylic complex [(κ^2-dtbpm)Rh(η^3-1-Ph-C_3H_4)] (**7**) is formed as the main product, which was identified by independent synthesis and structure determination.[12b] The excess of allylbenzene is isomerized to *trans*-β-methylstyrene by **7**.

In conclusion, the first neutral, three-coordinate alkylrhodium(I) complex with γ-C–H agostic stabilization of a 14-electron Rh center by a saturated alkyl ligand has been isolated and fully characterized. Its pronounced reactivity, which is based upon facile decoordination of the weakly bound hydrocarbon chain, makes it a suitable precursor for investigations of the d^8-ML$_3$ chemistry of rhodium and of unsaturated alkylrhodium complexes; it models intermediates in, for example, bond activation, hydroformylation, or polymerization reactions.

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[11] NMR data of **2** (for the data in [D$_8$]toluene see Supporting Information): ^{31}P{^{1}H} NMR (121 MHz, [D$_8$]THF, $-30\,^\circ$C): $\delta = 54.2$ (dd, ^1J(P,Rh) = 280.0, ^2J(P,P) = 22.1 Hz; P *cis* to Np); 21.6 (dd, ^1J(P,Rh) = 99.3, ^2J(P,P) = 22.1 Hz; P *trans* to Np); ^{1}H NMR (500 MHz, [D$_8$]THF, $-30\,^\circ$C): $\delta = 3.00$ (t, ^2J(H,P) = 7.3 Hz, 2H; PCH$_2$P), 1.42 (d, ^3J(H,P) = 12.7 Hz, 18H; *t*Bu *cis* to Np), 1.37 (d, ^3J(H,P) = 11.5 Hz, 18H; *t*Bu *trans* to Np), 0.83 (d, ^2J(H,P) = 2.2 Hz, 9H; $\mathrm{CH_2C(C}H_3)_3$, + ^{13}C satellites: ^1J(H,C) = 121 Hz), 0.40 (dm, ^3J(H,P) = 5.3 Hz, 2H; RhCH$_2$); ^{13}C{^{1}H} NMR (75 MHz, [D$_8$]THF, $-25\,^\circ$C): $\delta = 43.9$ (t, $J = 3.4$ Hz; CMe$_3$ from Np), 38.8 (d, $J = 10.6$ Hz; PCH$_2$P), 36.9 (m, $J = 5.3$ Hz; PCMe$_3$ *cis* to Np), 35.0 (dd, $J = 5.9$ Hz, $J = 3.0$ Hz; PCMe$_3$ *trans* to Np), 31.6 (m; $\mathrm{PC(}C\mathrm{H_3)_3}$), 28.7 (t, $J = 4.9$ Hz; (CH$_3$)$_3$, Np), 20.0 (m; RhC).

[12] a) Single crystals were obtained by slowly concentrating a solution of **2** in Et$_2$O at $-15\,^\circ$C by solvent evaporation. Crystal dimensions $0.37 \times 0.20 \times 0.10$ mm^3, monoclinic, space group $P2_1/n$, $Z = 4$, $a = 9.4062(1)$, $b = 19.1825(1)$, $c = 14.2169(2)$ Å, $\beta = 92.462(1)^\circ$, $V = 2562.85(5)$ Å^3, $\rho_{\mathrm{calcd}} = 1.240$ g cm^{-1}, $2\theta_{\mathrm{max}} = 55.0^\circ$, $\lambda(\mathrm{Mo_{K\alpha}}) = 0.71073$ Å, 0.3° ω scans, $T = 200$ K, 26061 reflections collected, 5883 unique, 4379 observed with $I > 2\sigma(I)$. Corrections for absorption were applied (program SADABS), $\mu = 0.795$ mm^{-1}, $T_{\mathrm{min}} = 0.75$, $T_{\mathrm{max}} = 0.94$. The structure was solved by Patterson methods and refined by full-matrix least-squares methods on F^2 (program SHELXTL (5.10)), 271 parameters refined. Np hydrogen atoms not localized but considered at calculated positions. Final agreement factors $R(F) = 0.040$, $wR(F^2) = 0.089$ for observed reflections. Largest peak and hole in the final difference map: 0.70 and -0.70 e Å^{-3}. b) Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-148676 (**2**), CCDC-148678 (**3**), CCDC-148677 (**6**), and CCDC-148679 (**7**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk). c) Structural data for **5**: C. Meier, PhD thesis, Technische Universität München (Germany), **1991**.

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[14] In all tetracoordinate complexes **3**–**6** the methyl proton resonance signals of the neopentyl ligand appear as a singlet. This, in line with ^{1}H{^{31}P} NMR data, excludes ^5J coupling of P1 with C3-H atoms through covalent bonds and establishes direct Rh-H-C contacts *trans* to P1 for **2**.

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[18] The computed T-Y-T in-plane inversion barrier for the model **2a** is 31.6 kcal mol^{-1} with a Y-shaped transition state (NIMAG = 1; 574.2 *i* cm^{-1}).[19]

[19] B3PW91; Stuttgart–Dresden basis sets with effective core potentials for Rh and P, 6-31G** basis sets for C and H; for details see Supporting Information. We thank Dr. E. Clot for technical assistance.

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$\mathrm{YBa_2Cu_3O_{6+\delta}}$ as an Oxygen Separation Membrane**

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High-T_c superconducting oxides exhibit fast oxygen transfer across the interface between gas and solid phase and diffusion in the bulk at elevated temperatures.[1, 2] This is of crucial importance to the fine-tuning of the superconductivity by intercalating oxygen into the oxides to oxidize the copper ions. The fast oxygen transport kinetics may also be used to develop oxygen-semipermeable dense membranes, which have potential applications in oxygen production and oxy-

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