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Communication

Controlled oxidative addition of amino acid esters to Rh(I)

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Abstract

The new sterically demanding phosphine 2-(di-*o*-tolylphosphino)phenol was prepared and used to create a series of esters with *N*-acylated amino acids. The phosphine-containing esters react within 30–60 min at room temperature with [(μ-Cl)Rh(cyclooctene)$_2$]$_2$ to give products of oxidative addition of the ester carbonyl–oxygen bond to the Rh center. The *N*-acyl carbonyl oxygen is bound to the Rh in these initial adducts, but is displaced upon addition of PMe_3. Remarkably, both initial products and their PMe_3 adducts are formed as single five-coordinate diastereomers in essentially quantitative yields. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

Both coordination [1] and organometallic [2] complexes of amino acids and peptides have been extensively studied, but these studies have so far focused on maintaining and using the robust amino acid framework [2], for instance, in the creation of chiral complexes or catalysts. For example, many organometallic fragments have been attached directly to N, O or S heteroatoms in amino acids and proteins from natural sources [2,3], or to P atoms in helical polypeptides containing unnatural amino acids [4]. Alternatively, organometallic reagents with reactive organic moieties at the periphery have been attached indirectly to heteroatoms using organic reactions such as amide bond formation [5]. Our interest in amino acid complexes has included direct π-complexation of amino acids and proteins in water or organic solvents [6,7], and diasteroselective formation [3y] and reactions [3w,x,8] of amino acid chelate complexes. However, none of these transformations has involved changes in the amino acid or peptide framework.

Although transformations of amino acids have been used to make chiral nitrogen-containing compounds (including ligands for chiral organometallic complexes [9]), with few exceptions, these reactions have not involved transition-metal organometallics. Castaño and Echavarren have reported the formation of nickelacycles from cyclic anhydrides derived from glutamic acid, reactions which involve oxidative addition of the anhydride to the Ni(0) center and subsequent decarbonylation [10]. Hungate et al. used $[CpFe(CO)_2]^-$ and mixed anhydrides of amino acid derivatives to create chiral acyl complexes for further asymmetric transformations [11]. In this communication, we report preliminary attempts to explore organometallic transformations of amino acid esters, illustrated in Scheme 1. Esterification of an *N*-acylated amino acid derivative **1** with a phosphine-containing alcohol such as **2** was anticipated to give **3**. Addition of a soft, low-valent metal complex to **3** would be expected to give **4**, which could undergo chelate-driven oxidative addition [12], providing **5**, and then chelate **6**. Alkyl migration in **6** would lead to **7**. In this paper, we report the clean formation of oxidative

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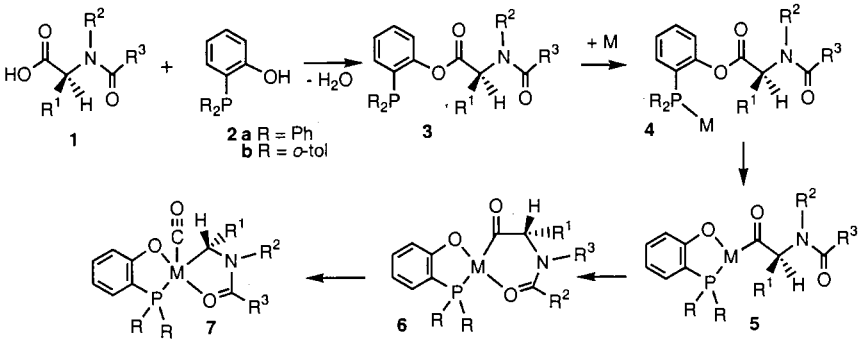


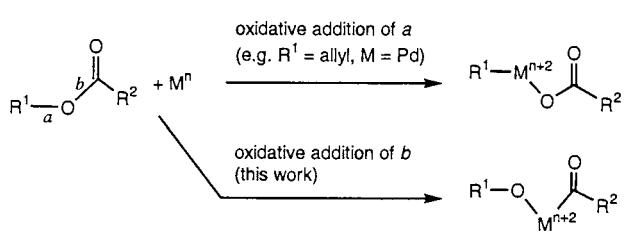
Scheme 1.

addition products of type **6** using Rh complexes. That these reactions proceed in essentially quantitative yields is significant because we have previously noted [13] that whereas addition of the alkyl C–O bond in allylic esters (Scheme 2a) is well known and leads to useful organic chemistry [14], the alternative addition of the carbonyl–oxygen bond in esters (Scheme 2b) is a rare, and usually messy reaction [15].

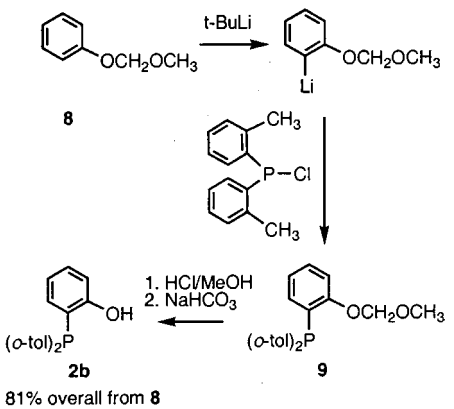
2. Results and discussion

Known 2-(diphenylphosphino)phenol **2a** [16] was used to esterify *N*-acetylglycine in the presence of dicyclohexylcarbodiimide (DCC) and 4-(*N*,*N*-dimethylamino)pyridine (DMAP) to give **3** ($R = Ph$, $R^1 = H$, $R^2 = CH_3$) in 79% yield [17]. Preliminary experiments [17] using this ester and the Ir(I) dimer $[(\mu\text{-}Cl)Ir(cyclooctene)_2]_2$ quickly led to two tentative conclusions: despite maintaining a stoichiometry of one phosphine per metal, there was a strong tendency to form mixtures of bis(phosphine) complexes, which then reacted rather slowly. Therefore, the subsequent experiments described here were conducted using the analogous Rh(I) dimer and bulkier phosphines. Because the cone angles of tris–(*o*-tolyl)phosphine and triphenylphosphine are 194 and 145°, respectively [18], the synthesis of the phenol **2b**, a new compound, was undertaken.

The requisite phosphine **2b** was readily made by adapting procedures used to make **2a** [16]. Directed deprotonation of methoxymethyl-protected phenol **8** with *t*-BuLi (Scheme 3) followed by addition of ClP(*o*-tolyl)$_2$ [19] gave crude **9**, which was treated with aqueous HCl and neutralized with bicarbonate to give **2b** as a white solid in 81% overall yield. Interestingly, Luo et al. found that treatment of other methoxymethyl-protected phenols bearing phosphine groups with HCl led to phosphonium salts because of the basicity of the phosphine moiety [20]. As the authors noted, in the previously reported preparation of **2a** [16], a base-neutralization step was omitted but the crude product was sublimed, consistent with known loss of HCl from phosphonium salts at elevated temperatures. In fact, whereas **2b** in our hands exhibited a single $^{31}P\{^1H\}$ resonance at δ −43.57 ppm, omission of the base neutralization step led to material (presumably the hydrochloride salt of **2b**, although this has not been investigated further) with a P nucleus absorbing at −15.38 ppm.

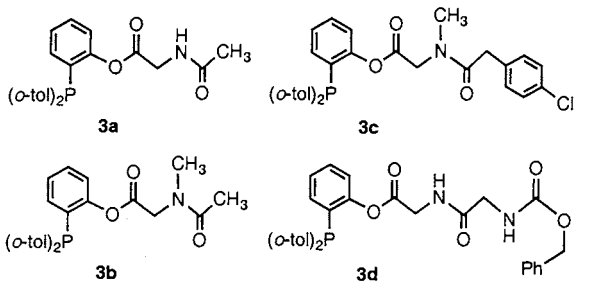


Scheme 2.



Scheme 3.

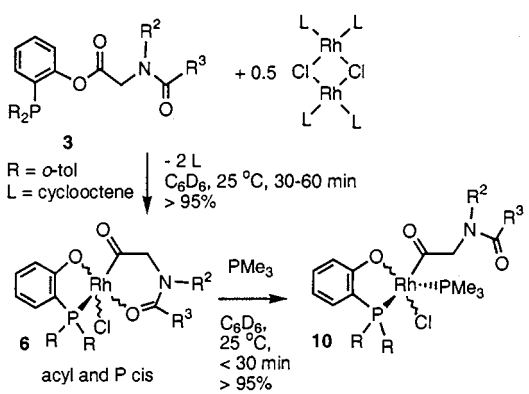
In order to explore the scope of oxidative addition chemistry, a variety of *N*-acylated amino acid derivatives **3** (Scheme 4) were made, representing the achiral acid glycine (**3a**), its *N*-alkylated derivative sarcosine (**3b**, **3c**), and the dipeptide glycylglycine (**3d**) protected with a *N*-terminal carbobenzoxy (Cbz) group. Typical DCC coupling of the *N*-acylated amino acids **1** and the phenol **2b** required about 20 h for completion, and yields ranged from 32 to 57%. A catalytic amount of DMAP [21,22] was added to inhibit *N*-acylurea forma-



Scheme 4.

tion from the activated *O*-acyl urea, because the attack of rather hindered nucleophile **2b** on the activated intermediate was feared to be slow.

To a room-temperature solution of the glycine ester **3a** and internal standard $[(CH_3)_3Si]_4C$ in C_6D_6 was added one equivalent (0.5 mol) of the rhodium (I) dimer $[(\mu\text{-Cl})Rh(cyclooctene)_2]_2$ [23]. Remarkably, within 30–60 min, one product formed in quantitative yield as determined by NMR integrations. The structure shown for **6a** (Scheme 5) is consistent with all spectroscopic data (Table 1). The $^{31}P\{^1H\}$-NMR spectrum of **6a** contains a doublet that is coupled to rhodium ($^1J_{RhP} = 174$ Hz) and provides the evidence for rhodium-bound phosphine [24]. The IR absorptions of **6a** at 1726 and 1584 cm^{-1} were consistent with metal-acyl [12b] and metal-coordinated amide [25], respectively. For comparison, the amide stretching frequency in starting material **3a** is 1678 cm^{-1}. In the $^{13}C\{^1H\}$-NMR spectrum of **6a**, the most downfield resonance at δ 209.35 (dd, $^1J_{RhC} = 34.0$ Hz, $^2J_{PC} = 4.4$ Hz) also confirms the existence of a metal-acyl, and hence oxidative addition of the ester acyl–oxygen bond to Rh [13]. Although the precise stereochemistry of **6** cannot be assigned, the small value of $^2J_{PC}$ shows unequivocally that the acyl and phosphine ligands are mutually *cis* [13,26]. The methylene protons (H_a, H_b) are diastereotopic ($^2J_{HH} = 11.0$ Hz), indicating a stereogenic element is present in **6a**. Both the sarcosine esters **3b** and **3c** reacted with $[(\mu\text{-Cl})Rh(cyclooctene)_2]_2$ to give single products **6b** and **6c** in quantitative yield. Very similar NMR and IR spectral data were obtained (Table 1).



Scheme 5.

Unfortunately, the available data do not allow us to determine the geometry of **6a**–**6c**. The literature contains many examples of stable five-coordinate rhodium acyl complexes, whether square pyramidal or trigonal bipyramidal [12b,27]; alternatively, cyclooctene could occupy a sixth site, making **6a**–**6c** octahedral. Some evidence for alkene involvement when a smaller alkene (and presumably better ligand) was involved came from reactions of the ethylene analog $[(\mu\text{-Cl})Rh(ethylene)_2]_2$ with **3a**; the resulting spectrum contained sharp resonances for **6a**, but a somewhat broadened resonance for ethylene. Upon standing in C_6D_6 for 12–15 h, the ^1H- and ^{31}P-NMR spectra of acyl complex **6a** degrade, and no identifiable features appear in replacement. Potential decomposition pathways include alkyl migration followed by β-hydride elimination involving the N–H group. In support of this idea, rhodium acyl complexes **6b** and **6c** featuring *N*-methyl groups were more stable in solution, persisting for 24–48 h. Nonetheless, complexes **6** could not be obtained in analytically pure form.

Therefore, trimethylphosphine was added to the complex **6a** to prevent decomposition by saturating the coordination sites. Once the phosphine is added to a solution of **6a** in benzene, the color changes from yellow to orange and spectral data (Table 1) implicate formation of a single product **10a** in greater than 95% yield. Similar results were obtained for **6b**–**d**, giving **10b**–**d**. Significantly, the PMe_3 adduct **10a** remains stable in solution for a week. The incoming trimethylphosphine ligand seemed to take up the site of the coordinated amide as revealed by the IR absorption at 1686 cm^{-1} (cf. 1678 cm^{-1} for free ligand **3a**). Also, the ^{31}P spectrum contained two separate resonances, both doublets of doublets ($^2J_{PP} = 389$ Hz, $^1J_{RhP} = 111$ Hz). Large splittings of each resonance indicate that the phosphines are mutually *trans* [23], with the acyl mutually *cis* to both phosphines: the $^{13}C\{^1H\}$-NMR data for the acyl carbon showed a larger splitting by Rh ($^1J_{RhC} = 34.0$ Hz) and two smaller and equal splittings by the P nuclei ($^2J_{PC} = {}^2J_{P'C} = 6.3$ Hz). The complexes are five coordinate, although at this point we do not know if they are square pyramidal or trigonal bipyramidal. Complex **10d** gives correct elemental analysis data, and its $^{31}P\{^1H\}$-NMR and IR data (see Section 4) are very similar to those for simpler analogues **10a**–**c**, but its ^1H-NMR spectrum exhibited several broadened resonances, perhaps because of hydrogen bonding of the three carbonyl groups and two NH groups in either an intramolecular or intermolecular sense.

Table 1
NMR data for Rh acyl complexes **6** and **10** in C_6D_6 (shifts δ in ppm, coupling constants J in Hz)

Complex	^{1}H-NMR				^{31}P{^{1}H}
	Methylenes	Ar–CH_3	Ar–*H*	*N*–CH_3, COCH_3 or P(CH_3)$_3$	
6a	3.43 (d, J = 11.0, 1 H) 4.04 (d, J = 11.0, 1 H)	2.55 (s, 3 H) 2.86 (s, 3 H)	6.47 (t, J = 7.5, 1 H) 6.63 (t, J = 5.7, 1 H) 6.73 (t, J = 7.5, 1 H) 6.82 (t, J = 7.8, 2 H) 6.95–7.20 (m, 4 H) 7.38 (t, J = 10.8, 2 H) 8.12 (dd, J = 12.3, 7.5, 1 H)	1.92 (s, 3 H)	+52.48 (d, J = 174)
6b	3.42 (d, J = 12.0, 1 H) 3.89 (d, J = 12.0, 1 H)	2.61 (s, 3 H) 2.93 (s, 3 H)	6.47 (t, J = 6.6, 1 H) 6.63 (t, J = 6.0, 1 H) 6.74 (t, J = 7.2, 1 H) 6.82 (t, J = 7.2, 1 H) 6.97–7.24 (m, 6 H) 7.42 (t, J = 6.9, 1 H) 8.22 (dd, J = 13.2, 7.5, 1 H)	1.71 (s, 3 H) 1.75 (s, 3 H)	+53.88 (d, J = 176)
6c	3.18 (d, J = 16.0, 1 H) 3.39 (d, J = 16.0, 1 H) 3.49 (d, J = 12.5, 1 H) 3.91 (d, J = 12.5, 1 H)	2.60 (s, 3 H) 2.86 (s, 3 H)	6.48 (t, J = 7.0, 1 H) 6.66 (t, J = 6.5, 1 H) 6.75 (t, J = 7.5, 1 H) 6.83 (t, J = 7.5, 1 H) 6.85–7.21 (m, 10 H) 7.42 (t, J = 8.0, 1 H) 8.23 (dd, J = 13.5, 8.0, 1 H)	1.89 (s, 3 H)	+53.81 (d, J = 177)
10a	3.83 (dd, J = 18.1, 5.7, 1 H) 4.34 (dd, J = 18.1, 7.2, 1 H)	2.34 (s, 3 H) 2.69 (s, 3 H)	6.51 (t, J = 6.6, 1 H) 6.78–6.87 (m, 3 H) 6.94–7.24 (m, 5 H) 7.36 (t, J = 8.1, 1 H) 7.61 (dd, J = 11.1, 8.4, 1 H)	1.28 (s, 3 H) 1.46 (dd, J = 11.4, 2.7, 9 H)	+32.46 (dd, J = 389, 111) +6.04 (dd, J = 389, 111)
10b	3.86 (d, J = 17.7, 1 H) 4.45 (d, J = 17.7, 1 H)	2.36 (s, 3 H) 2.71 (s, 3 H)	6.51 (t, J = 6.6, 1 H) 6.74–7.25 (m, 9 H) 7.34(t, J = 6.9, 1 H) 7.60 (dd, J = 10.8, 7.8, 1 H)	1.54 (s, 3 H) 1.58 (dd, J = 11.4, 3.0, 9 H) 1.64 (s, 3 H)	+32.10 (dd, J = 388, 113) +6.55 (dd, J = 388, 113)
10c	3.10 (s, 2 H) 3.87 (d, J = 17.0, 1 H) 4.48 (d, J = 17.0, 1 H)	2.33 (s, 3 H) 2.70 (s, 3 H)	6.50 (t, J = 7.2, 1 H) 6.70–7.25 (m, 13 H) 7.31 (t, J = 8.1, 1 H) 7.58 (dd, J = 11.1, 7.8, 1 H)	1.53 (dd, J = 10.8, 2.7, 9 H) 1.67 (s, 3 H)	+32.19 (dd, J = 386, 113) +6.49 (dd, J = 386, 113)

3. Conclusions

A new phenolic phosphine, **2b**, was prepared and its esters with four *N*-acylated amino acids were obtained. The steric hindrance about the phosphorus center controlled the stoichiometry of subsequent reactions with Rh(I) dimer [(μ-Cl)Rh(cyclooctene)$_2$]$_2$, so that within 1 h at room temperature, single products **6** were obtained in essentially quantitative yields. It is clear that in conversion of **3** to **6**, the ester CO–O bond has

been added to the Rh center to form five-coordinate (phenoxy)(acyl) complexes featuring a coordinated amide group. Addition of PMe_3 displaces the amide, giving five-coordinate acyls **10** in which the new ligand appears trans to the bulky phosphine. Future reports will attempt to clarify the bonding in **6** and **10** and the effects of an amino acid chiral center on the diastereoselectivity of the type of transformations described here.

4. Experimental

In addition to the general considerations reported in Ref. [13], some NMR spectra reported here were obtained using Varian Gemini 2000 200 MHz or Inova 500 MHz spectrometers.

4.1. 2-(Di-o-tolylphosphino)phenol (2b)

A 100 ml Schlenk flask was charged with **8** (0.500 g, 3.62 mmol) and dry diethyl ether (15 ml) under N_2 and the flask was immersed in a −40°C bath (CO_2–ethylene glycol). *t*-BuLi (2.13 ml of 1.70 M in hexane, 3.62 mmol) was added to the flask in one portion via syringe. An immediate white precipitate formed and the solution was stirred at −40°C for 1.5 h. A solution of $ClP(o\text{-tol})_2$ (0.900 g, 3.62 mmol) in diethyl ether (20 ml) was transferred to the Schlenk flask via cannula in one portion. After 1 h, the cooling bath was removed and the reaction was stirred at room temperature (r.t.) for 15 h. The reaction mixture was diluted with deoxygenated diethyl ether (20 ml) and washed with three portions of deoxygenated saturated sodium chloride (20 ml). The organic layers were dried over $MgSO_4$, filtered, and solvents were removed in vacuo. The resulting white solid was taken up in HCl-saturated methanol (100 ml) and the resulting solution stirred under N_2 for 24 h. The methanol was removed in vacuo, ethyl acetate (40 ml) was used to dissolve the solid, and the resulting solution was washed with saturated aqueous sodium bicarbonate (3 × 20 ml). The organic layer was dried over $MgSO_4$, filtered, and solvent removed from the filtrate in vacuo. The remaining white solid was purified by chromatography (5:1 dichloromethane–ethyl acetate) yielding a white solid (0.900 g, 81%). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 2.38 (s, 6 H), 6.25 (bs, 1 H), 6.85–6.90 (m, 4 H), 6.97 (dd, $J = 8.0$, 6.0 Hz, 1 H), 7.12 (t, $J = 7.2$ Hz, 2 H), 7.20–7.30 (m, 5 H) ppm. ^{13}C-NMR ($CDCl_3$, 101 MHz) δ 21.15 (d, $J = 20.4$ Hz), 115.52, 121.13 (d, $J = 2.5$ Hz), 126.28 (d, $J = 1.3$ Hz), 129.19, 130.37 (d, $J = 5.1$ Hz), 131.67, 132.59, 135.21 (d, $J = 4.4$ Hz), 142.33 (d, $J = 24.9$ Hz), 159.61 (d, $J = 17.8$ Hz) ppm. ^{31}P-NMR ($CDCl_3$, 162 MHz) δ −43.57 ppm. IR (KBr, cm^{-1}) 3385 (O–H), 1184 (C–O). Anal. Calc. for $C_{20}H_{19}OP$ (306.36): C; 78.40, H; 6.26. Found: C; 78.00, H; 6.33.

4.2. 2-(Di-o-tolylphosphino)phenol ester of N-acetylglycine (3a)

Phosphine **2b** (0.574 g, 1.88 mmol) was placed in a flask with deoxygenated dichloromethane and DMF (20 ml each). DMAP (0.023 g, 0.19 mmol) and *N*-acetylglycine (0.271 g, 2.31 mmol) were added to the flask and the solution was stirred at 0°C. A solution of DCC (0.427 g, 2.07 mmol) in dichloromethane (10 ml) was added via addition funnel over 30 min. The reaction was stirred and allowed to warm to r.t. overnight. The solution was filtered to remove DCU, dried over magnesium sulfate, filtered, and the solvents were removed on the high-vacuum line. The resulting white solid was purified by chromatography (20:1 dichloromethane–ethyl acetate) yielding a white solid (0.246 g, 32%). ^{1}H-NMR (C_6D_6, 300 MHz) δ 1.37 (s, 3 H), 2.41 (s, 6 H), 3.85 (d, $J = 5.4$ Hz, 2 H), 4.65 (m, 1 H), 6.76 (dt, $J = 7.8$, 1.8 Hz, 1 H), 6.86–7.10 (m, 11 H) ppm. ^{13}C-NMR (C_6D_6, 126 MHz) δ 21.18 (d, $J =$ 21.7 Hz), 22.89, 41.40 (d, $J = 1.6$ Hz), 122.55, 126.35, 126.85, 129.25, 130.28, 130.32, 133.26, 134.26 (d, $J =$ 3.3 Hz), 142.75 (d, $J = 27.3$ Hz), 152.79 (d, $J = 17.3$ Hz), 168.05, 169.99 ppm. ^{31}P-NMR (C_6D_6, 202.3 MHz) δ −31.82 ppm. IR (C_6D_6, cm^{-1}) 3437 (N–H), 1764 (C=O, ester), 1678 (C=O, amide). Anal. Calc. for $C_{24}H_{24}NO_3P$ (395.46): C; 70.55, H; 6.17, N; 3.64. Found: C; 71.08, H; 5.98, N; 3.46.

4.3. 2-(Di-o-tolylphosphino)phenol ester of N-acetyl-N-methylglyine (3b)

Using a procedure similar to that for **3a**, phosphine **2b** (0.417 g, 1.37 mmol) in dichloromethane (20 ml) and DMF (20 ml) was treated with DMAP (0.017 g, 0.14 mmol) and *N*-acetyl-*N*-methylglycine (0.180 g, 1.37 mmol) at 0°C, followed by a solution of DCC (0.311 g, 1.51 mmol) in dichloromethane (10 ml) added over 30 min. The reaction was stirred and allowed to warm to r.t. overnight. As in the preparation of **3a**, work-up followed by chromatography (dichloromethane) gave a white solid (0.327 g, 57%). NMR spectroscopy revealed the presence of major and minor rotamers in a ratio of approximately 2 to 1. ^{1}H-NMR (C_6D_6, 300 MHz) δ 2.03 (s, 1.0 H, minor), 2.05 (s, 2.0 H, major), 2.35 (s, 2.0 H, minor), 2.38 (s, 4.0 H, major), 2.79 (s, 1.0 H, minor), 2.81 (s, 2.0 H, major), 4.02 (s, 0.6 H, minor), 4.10 (s, 1.4 H, major), 6.70–6.80 (m, 1 H), 7.04–7.50 (m, 11 H) ppm. ^{31}P-NMR (C_6D_6, 202.3 MHz) δ −30.30 (major), −31.60 (minor) ppm. Anal. Calc. for $C_{25}H_{26}NO_3P$ (419.52): C, 70.95; H, 6.51; N, 3.74. Found: C, 71.37; H, 6.46; N, 3.64.

4.4. 2-(Di-o-tolylphosphino)phenol ester of N-(4-chlorophenyl)acetyl-N-methylglyine (**3c**)

Using a procedure similar to that for **3a**, phosphine **2b** (0.423 g, 1.39 mmol) in dichloromethane (10 ml) was treated with DMAP (0.0206 g, 0.169 mmol) and *N*-(4-chlorophenyl)acetyl-*N*-methylglycine (0.315 g, 1.30 mmol) at 0°C, followed by solid DCC (0.332 g, 1.61 mmol), using dichloromethane (ca. 1 ml) to rinse the weighing container. The reaction was stirred and allowed to warm to r.t. overnight. As in the preparation of **3a**, work-up followed by chromatography (ethyl acetate/dichloromethane) gave a white solid (0.3521 g, 51%). NMR spectroscopy revealed the presence of major and minor rotamers in a ratio of approximately 3.5 to 1. ^{1}H-NMR (C_6D_6, 500 MHz) δ 2.29 (s, 3 H, *N*–CH_3 of major), 2.31 (s, 6 H, Ar–CH_3 of minor), 2.37 (s, 6 H, Ar–CH_3 of major), 2.72 (s, 3 H, *N*–CH_3 of minor), 3.16 (s, 2 H, ArCH_2CO of major), 3.29 (s, 2 H, ArCH_2CO of minor), 3.55 (s, 2 H, NCH_2CO of minor), 3.94 (s, 2 H, NCH_2CO of major), 6.70–7.10 (m, 16 H for both major and minor) ppm. ^{31}P-NMR (C_6D_6, 80.95 MHz) δ −31.78 ppm (only one peak seen).

4.4.1. 2-(Di-o-tolylphosphino)phenol ester of CbzGlyGly (**3d**)

At 0°C, to a solution of phosphine **4** (0.518 g, 1.70 mmol) in dichloromethane (30 ml) and DMF (10 ml) was added DMAP (0.021 g, 0.17 mmol) and CbzGlyGlyOH (0.480 g, 1.71 mmol), followed by a solution of DCC (0.386 g, 1.87 mmol) in dichloromethane (20 ml) according to the procedure used for **7a**. The crude solid product was purified by chromatography (20:1 dichloromethane–ethyl acetate) yielding a white solid (0.416 g, 43%). ^{1}H-NMR (C_6D_6, 300 MHz) δ 2.40 (s, 6 H), 3.35 (d, $J = 4.8$ Hz, 2 H), 3.75 (d, $J = 5.7$ Hz, 2 H), 4.81 (bs, 1 H), 5.02 (s, 2 H), 5.42 (t, $J = 5.7$ Hz, 1 H), 6.76 (dt, $J = 6.6$, 1.5 Hz, 1 H), 6.70–7.25 (m, 16 H) ppm. ^{13}C-NMR ($CDCl_3$, 101 MHz) δ 21.11 (d, $J = 22.2$ Hz), 41.03, 44.25, 67.25, 122.43, 122.46, 126.27, 126.84, 128.19 (d, $J = 13.1$ Hz), 128.54, 128.61, 129.10, 130.20, 130.24, 133.15, 133.23, 134.24 (d, $J = 2.7$ Hz), 136.03, 142.67 (d, $J = 27.1$ Hz), 152.67 (d, $J = 17.3$ Hz), 156.44, 167.63, 168.89 ppm. ^{31}P-NMR ($CDCl_3$, 161.9 MHz) δ −31.01 ppm. IR (C_6D_6, cm^{-1}) 3416 (N–H), 1774 (C=O, ester), 1734 (C=O, carbamate), 1697 (C=O, amide). Anal. Calc. for $C_{32}H_{31}N_2O_5P$ (554.62): C, 69.29, H, 5.65, N, 5.05. Found: C, 69.05; H, 5.78; N, 5.20.

4.5. Complex **10a**

In the glove-box, **3a** (0.0500 g, 0.124 mmol) was added to benzene (10 ml) in a 50 ml round bottom flask. The dimer, [(μ-Cl)Rh(cyclooctene)$_2$]$_2$, (0.0440 g, 0.0618 mmol) was added and the dark orange colored reaction was stirred for 30 min until a yellow color had developed. The yellow reaction mixture was stirred an additional 30 min to ensure complete reaction before PMe_3 (0.0094 g, 0.12 mmol) was added in one portion and the solution immediately turned orange. The solvent volume was reduced to 5 ml and hexane was added to induce precipitation. The precipitate was filtered and washed with hexane (3 × 5 ml) yielding a bright yellow solid (0.072 g, 94%). NMR data: see Table 1 and text. IR (C_6D_6, cm^{-1}) 3432 (N–H), 1709 (C=O, acyl), 1686 (C=O, amide). Anal. Calc. For $C_{26}H_{33}ClNO_3P_2Rh$ (618.81): C, 52.31, H, 5.38, N, 2.26. Found: C, 52.54; H, 5.45; N, 2.28.

4.6. Complex **10b**

In the glove-box, following the procedure used to make **10a**, **3b** (0.0622 g, 0.149 mmol) in benzene (10 ml) was reacted with [(μ-Cl)Rh(cyclooctene)$_2$]$_2$, (0.0533 g, 0.0743 mmol) for a total of 60 min before PMe_3 (0.0113 g, 0.149 mmol) was added. After work-up, bright yellow solid (0.091 g, 97%) was obtained. NMR data: see Table 1 and text. IR (C_6D_6, cm^{-1}) 1711 (C=O, Rh–acyl), 1657 (C=O, amide). Anal. Calc. for $C_{28}H_{35}ClNO_3P_2Rh$ (632.84): C, 53.14, H, 5.59, N, 2.21. Found: C, 52.91; H; 5.45; N, 2.28.

4.7. Complex **10d**

In the glove-box, following the procedure used to make **10a**, **3d** (0.0680 g, 0.119 mmol) in benzene (10 ml) was reacted with [(μ-Cl)Rh(cyclooctene)$_2$]$_2$, (0.0430 g, 0.0596 mmol) for a total of 60 min before PMe_3 (0.0091 g, 0.12 mmol) was added. After work-up, the yield of bright yellow solid was 0.090 g (97%). Partial data: ^{31}P{^{1}H}-NMR (MHz) δ 5.69 (dd, $J = 387$, 114 Hz), 32.59 (dd, $J = 387$, 110 Hz) ppm. IR (C_6D_6, cm^{-1}) 1734 (acyl), 1690 and 1709 (amide and carbamate). Anal. Calc. For $C_{35}H_{40}ClN_2O_5P_2Rh$ (783.97): C, 53.62, H, 5.15, N, 3.57. Found: C, 53.40; H, 5.32; N, 3.47.

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