Supplementary Material (ESI) for Chemical Communications

Stereocontrol mechanism in CO/*p*-methylstyrene copolymerisation catalysed by aryl-α-diimine Pd(II) complexes

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General considerations

All manipulations were carried out under a nitrogen atmosphere by using Schlenk techniques. Solvents were dried by standard methods and freshly distilled under nitrogen. *p*-Methylstyrene (Aldrich) was dried over calcium hydride and distilled before use. Carbon monoxide (Cp grade 99.99%) was supplied by Air Liquide. CP grade chemicals were used as received unless otherwise stated. Chloroform-*d* and methylene chloride-d_2 were degassed and stored over 3Å molecular sieves. Complexes $Pd(CH_3)(Cl)(Ar–N=C(Me)–C(Me)=N–Ar)$ (**4**: Ar = 4-$(OCH_3)C_6H_4$; **5**: Ar = 2,6-$(CH_3)_2C_6H_3$) were synthesized according to literature methods for analogous compounds.[1] Compound $NaBAr'_4$ (Ar' = 3,5-$(CF_3)_2C_6H_3$) was synthesized as previously reported.[2] Elemental analyses (C, H, N) were carried out with a Fisons Instruments 1108 CHNS-O Elemental Analyser. Infrared spectra were measured in the range 4000-600 cm^{-1} on a Nicolet FT-IR Avatar 360 spectrometer. NMR spectra were measured on a Bruker Advance 200 spectrometer with a multinuclear 5 mm probehead. ^1H and ^{13}C NMR chemical shifts are relative to TMS and were measured using the residual proton or carbon resonance of the deuterated solvents.

In compounds **6-12** the counterion $[BAr'_4]^-$ gives a pattern of NMR signals with the following typical chemical shifts: ^1H NMR ($CDCl_3$, 293 K): δ = 7.71 (8H, s, Ar'-H_o); 7.54 (4H, s, Ar'-H_p). ^{13}C NMR ($CDCl_3$, 293 K): δ = 161.7 (q, ^1J (C,B) = 49.3 Hz, Ar'-C_i); 134.8 (s, Ar'-C_o); 128.8 (q, ^2J (C,F) = 31.2 Hz; Ar'-C_m); 124.6 (q, ^1J (C,F) = 270.8 Hz, CF_3); 117.5 (s, Ar'-C_p).

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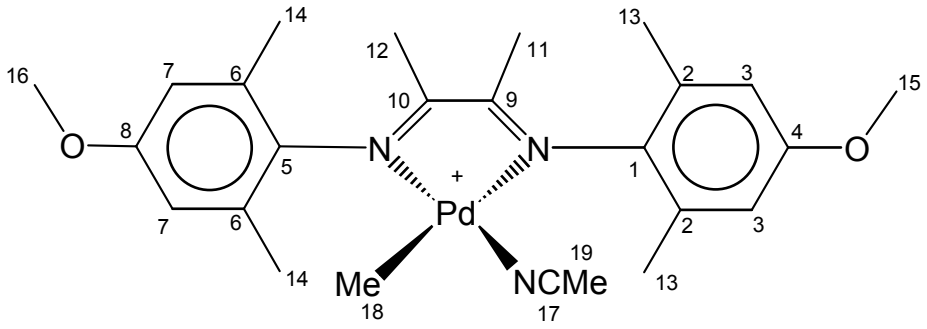
[1] R. van Asselt, E. E. C. G.; Gielens, R. E. Rülke, K. Vrieze and C. J. Elsevier, *J. Am. Chem. Soc.,* 1994, **116**, 977.

[2] (a) S. R. Bahr and P. Boudjouk, *J. Org. Chem.* 1992, **57**, 5545. (b) M. Brookhart, B. Grant and A. Volpe, *Organometallics* 1992, **11**, 3920.

For the CO/*p*-methylstyrene copolymer characterization, NMR samples were prepared by dissolving about 35 mg of the copolymer in a mixture of $(CF_3)_2CHOH$ (HFIP) and $CDCl_3$ (1/1, v/v). The molecular weights (M_w) of polymers and the molecular weight distributions (M_w/M_n) were determined by gel permeation chromatography versus polystyrene standards. The analyses were recorded with a Knauer HPLC (K-501 Pump, K-2501 UV-detector) with a PLgel 5 mm 10^4 Å GPC column and chloroform as solvent (flow rate: 0.6 mL min^{-1}). Samples were prepared by dissolving 2 mg of the copolymer in $CHCl_3$ (10 mL). The statistical calculations were performed using the Bruker Chromstar software program.

Numbering scheme for the assignment of the NMR resonances of complexes 2-3



Preparation and characterization of complex 2

A 25 mg (0.09 mmol) sample of $AgPF_6$ was added to a dichloromethane/acetonitrile (5:1) solution (6 mL) of **4** (40 mg, 0.08 mmol) cooled at 0 °C. The reaction mixture was allowed to react for 2 h and filtered through Celite to remove AgCl. Solvent was then evaporated in vacuum, and the resulting solid was washed with hexane (2 × 5 mL). A 49 mg (0.08 mmol, yield 93%) sample of **2** was collected as a yellow powder. IR (film): 2328, 2301 ($CH_3C{\equiv}N$), 1609 (C=N) cm^{-1}. ^1H NMR ($CDCl_3$, 293 K): δ 7.12-6.98 (8H, m, H2, H3, H6, H7), 3.85 (3H, s, H15 or H16), 3.84 (3H, s, H15 or H16), 2.32 (3H, s, H11 or H12), 2.25 (3H, s, H12 or H11), 2.02 (3H, s, H19), 0.47 (3H, s, H18). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293 K): δ 181.8 (s, C9 or C10), 172.1 (s, C10 or C9), 158.7 (s, C4 or C8), 158.3 (s, C8 or C4), 139.1 (s, C1 or C5), 138.5 (s, C5 or C1), 122.8 (s, C3 or C7), 122.6 (s, C7 or C3), 114.8 (s, C17), 114.5 (s, C2 or C6), 114.3 (s, C6 or C2), 55.6 (s, C15 o C16), 55.5 (s, C16 o C15), 21.1 (s, C11 or C12), 19.3 (s, C12 or C11), 5.5 (s, C19), 2.1 (s, C18). Anal Calcd for $C_{21}H_{26}F_6N_3O_2PPd$ (603.83): C, 41.77; H, 4.34; N, 6.96. Found: C, 41.85; H, 4.35; N, 6.95.

Preparation and characterization of complex 3

Complex **3** was synthesized according to the procedure described for **2** using 189 mg (0.42 mmol) of **5** and 109 mg (0.43 mmol) of $AgPF_6$. A 260 mg (0.40 mmol, yield 96 %) sample of **3** was collected as a

yellow powder. IR (film): 2330, 2303 ($CH_3C{\equiv}N$), 1611 (C=N) cm^{-1}. ^1H NMR ($CDCl_3$, 293 K): δ 7.16 (6H, m, H3, H4, H7, H8), 2.29 (6H,s, H13 or H14), 2.25 (3H, s, H11 or H12), 2.23 (3H, s, H12 or H11), 2.21 (6H, s, H14 or H13), 1.85 (3H, s, H19), 0.29 (3H, s, H18). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 290 K): δ 181.4 (s, C9 or C10), 173.3 (s, C10 or C9), 142.7 (s, C1 or C5), 142.6 (s, C5 or C1), 128.6 (s, C3 or C7), 128.4 (s, C7 or C3), 128.3 (s, C4 or C8), 127.6 (s, C4 or C8), 127.5 (s, C2 or C6), 126.9 (s, C6 or C2), 121.3 (s, C17), 19.8 (s, C11 or C12), 18.8 (s, C12 or C11), 17.8 (s, C13 or C14), 17.7 (s, C14 and C13), 4.3 (s, C19), 1.9 (s, C18). Anal Calcd for $C_{21}H_{26}F_6N_3O_2PPd$ (642.98): C, 48.57; H, 5.80; N, 6.54. Found: C, 48.60; H, 5.83; N, 6.60.

CO/*p*-Methylstyrene copolymerization catalyzed by complexes 2 and 3:

Complex **2** or **3** (0.14 mmol) were dissolved in dichloromethane (5 mL) at 17 °C under nitrogen, then *p*-methylstyrene (5.5 mL, 42 mmol) was added (olefin/palladium molar ratio: 300:1). The resulting solution was transferred into a thermostated Schlenk flask equipped with a carbon monoxide gas line and a tank for the CO. The solution was allowed to react for 51 h at 17 °C. The resulting gray polymer was precipitated with methanol and washed with methanol. To remove metallic palladium, the polymer was redissolved in chloroform, filtered through Celite, precipitated with methanol, washed with methanol, and dried under vacuum. Since in both cases a mixture of copolymer (96%) and poly(*p*-methylstyrene) (4%) was obtained from the reaction, diethyl ether was added to the mixture in order to extract the homopolymer. The resulting suspension was stirred vigorously for several hours and the ether solution was decanted off from the powder.

When catalyst **2** was used 220 gCP/gPd (grams of copolymer for gram of palladium) were obtained. The ^1H and ^{13}C NMR spectroscopic data were consistent with the isolation of atactic alternating CO/*p*-methylstyrene copolymer.[3] The relative percentages of the triads, estimated from the ^{13}C NMR spectrum in the region of the *ipso*-carbon atom, were *ll* : *ul*/*lu* : *uu* = 25 : 53 : 22. Anal Calcd for $(C_{10}H_{10}O)_n$: C, 82.16; H, 6.89. Found: C, 82.36; H, 6.91. M_w = 15000; M_w/M_n = 1.7.

When catalyst **3** was used 38 gCP/gPd were obtained. The ^1H and ^{13}C NMR spectroscopic data were consistent with the isolation of predominantly isotactic alternating CO/*p*-methylstyrene copolymer.[3] The relative percentages of the triads, estimated from the ^{13}C NMR spectrum in the region of the *ipso*-carbon atom, were *ll* : *ul*/*lu* : *uu* = 74 : 25 : 1. Anal Calcd for $(C_{10}H_{10}O)_n$: C, 82.16; H, 6.89. Found: C, 82.33; H, 6.88. M_w = 9200; M_w/M_n = 1.3.

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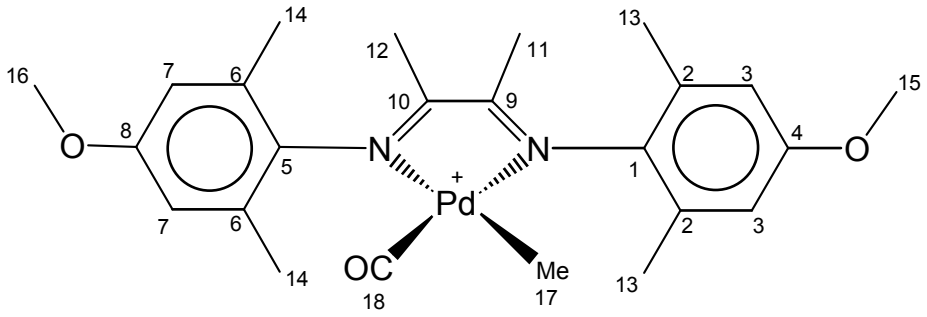
[3] B. Binotti, G. Bellachioma, G. Cardaci, C. Carfagna, C. Zuccaccia and A. Macchioni, *Chem. Eur. J.,* 2007, **13**, 1570.

Numbering scheme for the assignment of the NMR resonances of complexes 6-7



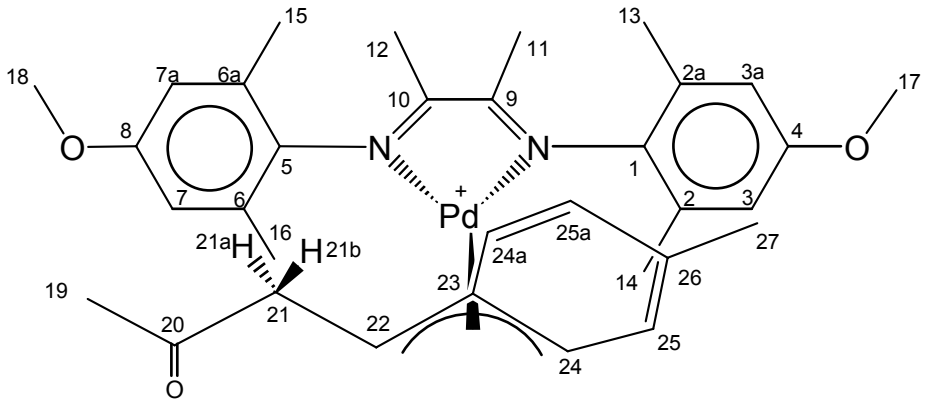
Preparation and characterization of complex 6

A 50 mg (0.111 mmol) sample of **4** and a 98.5 mg (0.111 mmol) sample of $NaBAr'_4$ were dissolved at –30 °C in dichloromethane (3 mL) previously saturated with CO. The reaction mixture was slowly warmed to 0°C and filtered through Celite to remove NaCl. Solvent was then evaporated in vacuum, and the resulting red oil was washed with hexane (3 x 4 mL). A 90 mg (0.069 mmol, yield 62 %) sample of **6** was collected as a red powder. IR (film): 2132 (C≡O); 1607 (C=N) cm^{-1}. ^1H NMR ($CDCl_3$, 293 K): δ 7.02 (2H, d, *J* = 8.7 Hz, H6), 6.98 (4H, s br, H2 and H3), 6.75 (2H, d, *J* = 8.7 Hz, H7), 3.83 (6H, s, H15 and H16), 2.27 (6H, s br, H11 and H12), 0.87 (3H, s, H17). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293 K): δ 184.0, 174.2 (s, C9 and C10), 173.1 (s, C18), 160.1 (s, C4), 159.5 (s, C8), 139.3 (s, C5), 135.8 (s, C1), 121.9 (s, C2 and C6), 115.3 (s, C3 and C7), 55.5 (s, C15 and C16), 21.4, 19.5 (s, C11 and C12), 8.8 (s, C17). Anal Calcd for $C_{52}H_{35}F_{24}N_2O_3BPd$ (1309.04): C, 47.71; H, 2.69; N, 2.14. Found: C, 47.9; H, 2.8; N, 2.0.

Preparation and characterization of complex 7

Complex **7** was synthesized according to the procedure described for **6** using 50 mg (0.111 mmol) of **5** and 98.6 mg (0.111 mmol) of $NaBAr'_4$. A 138 mg (0.106 mmol, yield 95%) sample of **7** was collected as an orange powder. IR (film): 2138 (C≡O); 1610 (C=N) cm^{-1}. ^1H NMR ($CDCl_3$, 253 K): δ 7.16 (6H, m, H3, H4, H7 and H8), 2.25, 2.16 (3H each, s, H11 and H12), 2.16 (6H, s, H14), 2.04 (6H, s, H13), 0.68 (3H, s, H17). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 253 K): δ 183.4, 175.3 (s, C9 and C10), 173.7 (s, C20), 144.3 (s, C5), 139.8 (s, C1), 129.5 (s, C7) 129.4 (s, C3), 129.0, 128.7 (s, C4 and C8), 127.4 (s, C2), 125.7 (s, C6), 20.3, 18.7 (s, C11 and C12), 17.8 (s, C14), 17.6 (s, C13), 8.4 (s, C17). Anal Calcd for $C_{54}H_{39}F_{24}N_2OBPd$ (1305.10): C, 49.70; H, 3.01; N, 2.15. Found: C, 49.8; H, 3.2; N, 2.1.

Numbering scheme for the assignment of the NMR resonances of complexes 8-9



Preparation and characterization of complex 8

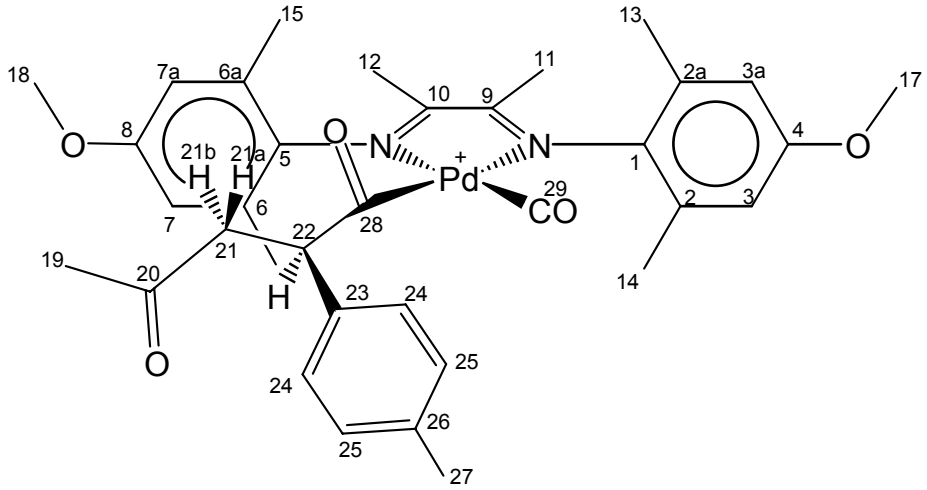
A 62.7 mg (0.048 mmol) sample of **6** was dissolved in 1 mL of chloroform at 0°C; *p*-methylstyrene (6.5 μL, 0.049 mmol) was then added. After 1 h the solution was filtered trough Celite and the solvent was evaporated in vacuum. The resulting oil was washed with hexane (2 x 3 mL) to yield complex **8** (65.3 mg, 0.046 mmol, yield 96%) as a red powder. IR (film): 1719 (C=O); 1607 (C=N) cm^{-1}. ^{1}H NMR ($CDCl_3$, 253 K): δ 7.05 (2H, d, *J* = 8.7 Hz, H7a and H7), 6.94 (4H, d, *J* = 8.7, H6a, H6, H3a and H3), 6.75 (2H, d, *J* = 7.3 Hz, H25a and H25), 6.44 (2H, d, *J* = 8.7 Hz, H2a and H2), 6.40 (2H, d, *J* = 7.3 Hz, H24a and H24), 3.84 (6H, s, H17 and H18), 3.15 (1H, dd, *J* = 2.5 Hz and *J* = 9.6 Hz, H22), 2.57 (1H, dd, *J* = 9.6 Hz and *J* = 18.9 Hz, H21b), 2.17, 2.09 (3H each, s, H11 and H12), 2.02 (3H, s, H19), 1.90 (3H, s, H27), 1.51 (1H, dd, *J* = 2.5 Hz and *J* = 18.9 Hz, H21a). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 253 K): δ 209.3 (s, C20), 176.2, 172.8 (s, C9 and C10), 159.0, 158.8 (s, C8 and C4), 141.0 (s, C26), 139.7 (s, C5), 138.4 (s, C1), 133.8 (s, C25a and C25), 122.0 (s, C6a and C6), 121.1 (s, C2a and C2), 118.9 (s, C23), 114.9 (s br, C7a and C7), 114.6 (s, C3a and C3), 109.8 (s br, C24a and C24), 55.7, 55.6 (s, C17 and C18), 53.1 (s, C22), 43.7 (s, C21), 29.7 (s, C19), 22.2 (s, C27), 20.1, 19.5 (s, C11 and C12). Anal Calcd for $C_{61}H_{45}F_{24}N_2O_3BPd$ (1427.22): C, 51.34; H, 3.18; N, 1.96. Found: C, 51.1; H,3.2; N, 1.8.

Preparation and characterization of complex 9

Complex **9** was synthesized according to the procedure described for **8** using 85 mg (0.065 mmol) of **7** and 8.5 μL (0.065 mmol) of *p*-methylstyrene. A 77 mg (0.054 mmol, yield 84%) sample of **9** was collected as an orange powder. IR (film): 1719 (C=O); 1610 (C=N) cm^{-1}. ^{1}H NMR ($CDCl_3$, 293 K): δ 7.22 (5H, m, H8, H7a, H7, H4, H3), 7.05 (1H, m, H3a), 6.54 (2H, d, *J* = 7.3 Hz, H25a and H25), 6.33 (2H, d, *J* = 7.3 Hz, H24a and H24), 3.17 (1H, dd, *J* = 4.1 Hz and *J* = 9.6 Hz, H22), 2.31 (1H, dd, *J* = 9.6

Hz and *J* = 18.7 Hz, H21b), 2.26 (3H, s, H15 or H16), 2.17 (3H, s, H14), 2.09 (3H, s, H12), 2.01 (3H, s, H11), 1.91 (3H, s, H16 or H15), 1.89 (3H, s, H19), 1.79 (3H, s, H27), 1.37 (3H, s, H13), 1.12 (1H, dd, *J* = 4.1 Hz and *J* = 18.7 Hz, H21a). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 293 K): δ 203.3 (s, C20), 176.3, 173.6 (s, C9 and C10), 143.9 (s, C5), 142.8 (s, C1), 141.6 (s, C26), 134.5 (s, C25a and C25), 129.7 (s, C7a or C7), 129.1 (s, C3), 128.9 (s, C7 or C7a), 128.8 (s, C3a), 127.8 (s, C8), 127.3 (s, C4), 127.2, 126.5 (s, C6a and C6), 125.8 (s, C2a), 125.6 (s, C2), 116.8 (s, C23), 106.1 (s br, C24a and C24), 55.5 (s, C22), 40.6 (s, C21), 29.6 (s, C19), 21.9 (s, C27), 18.7, 18.4 (s, C11 and C12), 17.8 (s, C15 or C16), 17.5 (s, C14), 17.0 (s, C15 or C16), 16.4 (s, C13). Anal Calcd for $C_{63}H_{49}F_{24}N_2OBPd$ (1423.28): C, 53.17; H, 3.47; N, 1.97. Found: C, 53.4; H, 3.2; N, 2.1.

Numbering scheme for the assignment of the NMR resonances of complexes 10-11



Preparation and characterization of complex 10

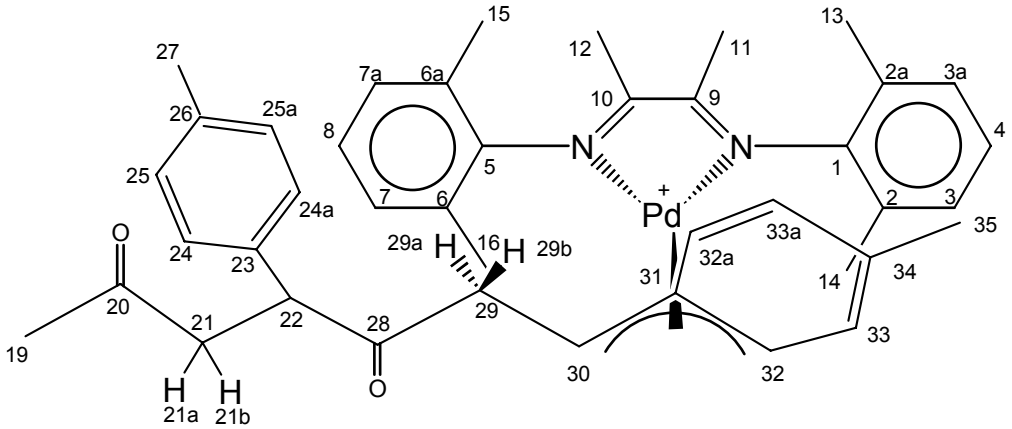
Complex **8** (65.0 mg, 0.046 mmol) was dissolved in $CDCl_3$ (0.5 mL) in an NMR tube. Carbon monoxide was bubbled through the solution for 5 minutes at –20°C. NMR analysis at the same temperature revealed the quantitative formation of complex **10**. Moeover, spectra show that at 20°C complex **10** was partially decarbonylated to complex **8**, with an equilibrium ratio of 75/25. IR (CD_2Cl_2): 2130 (C≡O); 1721 (Pd(C=O) and (C=O)Me); 1606 (C=N) cm^{-1}. ^{1}H NMR ($CDCl_3$, 223 K): δ 7.12 (2H, d, *J* = 8.0 Hz, H25a and H25), 7.02 (2H, d, *J* = 8.0 Hz, H24a and H24), 6.94 (3H, m, H6a, H7a and H7), 6.80 (4H, s, H2a, H2, H3a and H3), 6.77 (1H, m, H6), 3.79, 3.70 (3H each, s, H17 and H18), 4.29 (1H, dd, *J* = 1.5 Hz and *J* = 10.0 Hz, H22), 2.77 (1H, dd, *J* = 10.0 Hz and *J* = 18.6 Hz, H21a), 2.22, 2.17 (3H each, s, H11 and H12), 2.22 (3H, s, H27), 1.93 (3H, s, H19), 1.84 (1H, dd, *J* = 1.5 Hz and *J* = 18.6 Hz, H21b). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 223 K): δ 213.7 (s, C28) 205.1 (s, C20), 181.4, 171.4 (s, C9 and C10), 171.0 (s, C29), 159.6, 159.2 (s, C8 and C4), 139.7 (s, C26), 138.4, 138.0 (s, C5 and C1), 130.7 (s, C25a and C25), 129.7 (s, C24a and C24), 128.7 (s, C23), 122.4 (s br, C6a and C6), 121.8 (s, C2a and C2), 115.6 (s br, C7a and

C7), 114.9 (s, C3a and C3), 60.5 (s, C22), 55.74, 55.72 (s, C17 and C18), 45.1 (s, C21), 30.1 (s, C19), 21.4 (s, C27), 21.4, 20.1 (s, C11 and C12).

Preparation and characterization of complex 11

Complex **9** (77.0 mg, 0.054 mmol) was dissolved in $CDCl_3$ (0.5 mL) in an NMR tube. Carbon monoxide was bubbled through the solution for 5 minutes at –20°C. The solution was allowed to stand at –20 °C for 48 hours and then monitored at the same temperature through NMR, showing the formation of a mixture of compounds **9/11** with an equilibrium ratio of 70/30. At 20°C this equilibrium is completely shifted towards the η^3-allyl compound **9**. ^{1}H NMR ($CDCl_3$, 253 K): δ 7.20-7.03 (6H, m, H8, H7a, H7, H4, H3a and H3), 7.14 (2H, d, *J* = 8.0 Hz, H25a and H25), 7.01 (2H, d, *J* = 8 Hz, H24a and H24), 4.20 (1H, dd, *J* = 1.9 Hz and *J* = 10.2 Hz, H22), 2.72 (1H, dd, *J* = 10.2 Hz and *J* = 18.6 Hz, H21a), 2.39, 2.13, 2.11, 2.09 (3H each, s, H13, H14, H15 and H16) 2.22, 2.13 (3H each, s, H11 and H12), 2.22 (3H, s, H27), 1.92 (3H, s, H19), 1.67 (1H, dd, *J* = 1.9 Hz and *J* = 18.6 Hz, H21b). ^{13}C{^{1}H} NMR ($CDCl_3$, 253 K): δ 210.7 (s, C28), 204.5 (s, C20), 180.4, 173.9 (s, C9 and C10), 170.6 (s, C29), 143.6, 142.5 (s, C5 and C1), 140.0 (s, C26), 130.7 (s, C25a and C25), 129.9, 129.6, 129.4 (s, C7a, C7, C3a and C3), 129.6 (s, C24a and C24), 128.63 (s, C23), 128.58, 128.49 (s, C8 and C4), 128.2, 126.9, 125.4, 125.3 (s, C6a, C6, C2a and C2), 59.9 (s, C22), 44.6 (s, C21), 29.8 (s, C19), 21.4 (s, C27), 19.7, 19.0 (s, C11 and C12), 17.9, 17.8 (s, C13, C14, C15 and C16).

Numbering scheme for the assignment of the NMR resonances of complex 12:



Preparation and characterization of complex 12

Complex **9** (77.0 mg, 0.054 mmol) was dissolved in $CDCl_3$ (0.5 mL) in an NMR tube. Then carbon monoxide was bubbled through the solution for 5 minutes and *p*-methylstyrene (7 μL, 0.053 mmol) was

added. The solution was allowed to stand at –20°C for 20 days and then filtered trough Celite. The solvent was evaporated in vacuum and the resulting oil was washed with hexane (2 x 3 mL) to yield an orange powder (80 mg), which was shown to be a 25/75 mixture of componds **9/12**. ^{1}H NMR ($CDCl_3$, 293 K): δ 7.24-7.20 (2H, m, H8 and H4), 7.17 (2H, d, *J* = 8.1 Hz, H25a and H25), 7.11-6.98 (4H, m, H7a, H7, H3a and H3), 6.90 (2H, d, *J* = 8.1 Hz, H24a and H24), 6.59 (2H, d, *J* = 7.6 Hz, H33a and H33), 6.45 (2H, d, *J* = 7.6 Hz, H32a and H32), 3.84 (1H, dd, *J* = 2.9 Hz and *J* = 11.2 Hz, H22), 3.36 (1H, dd, *J* = 11.2 Hz and *J* = 18.4 Hz, H21a or H21b), 2.81 (1H, dd, *J* = 4.3 Hz and *J* = 11.2 Hz, H30), 2.60 (1H, dd, *J* = 2.9 Hz and *J* = 18.4 Hz, H21a or H21b), 2.53 (1H, dd, *J* = 11.2 Hz and *J* = 17.4 Hz, H29b), 2.22 (3H, s, H27), 2.16 (3H, s, H15 or H16), 2.13 (3H, s, H14), 2.11 (3H, s, H12), 2.04 (3H, s, H11), 1.95 (3H, s, H16 or H15), 1.92 (3H, s, H19), 1.80 (3H, s, H35), 1.38 (3H, s, H13), 1.27 (1H, dd, *J* = 4.3 Hz and *J* = 17.4 Hz, H29a). ^{13}C{^{1}H} NMR ($CDCl_3$, 293 K): δ 207.3 (s, C20), 204.8 (s, C28), 176.0, 173.5 (C9 and C10), 144.1 (s, C5), 142.7 (s, C1), 141.6 (s, C34), 137.9 (s, C26), 134.4 (s, C33a and C33), 132.9 (s, C23), 129.8 (s, C25a and C25), 129.3, 128.80 (s, C7a, C7), 129.2 (s, C3a), 129.1 (s, C8), 128.77 (s, C3), 127.9 (s, C24a and C24), 127.3 (s, C4), 126.5, 126.1 (s, C6a and C6), 125.8 (s, C2a), 125.5 (s, C2), 117.3 (s, C31), 106.3 (s br, C32a and C32), 56.1 (s, C30), 52.6 (s, C22), 47.6 (s, C21), 39.7 (s, C29), 29.4 (s, C19), 22.0 (s, C35), 21.0 (s, C27), 18.5, 18.4 (s, C11 and C12), 17.7 (s, C15 or C16), 17.5 (s, C14), 17.1 (s, C15 or C16), 16.5 (s, C13).