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A convenient synthesis of high-loaded palladium(II) ROMP polymers

D. Christopher Braddock,[a,*] David Chadwick[b] and Eduard Lindner-López[b]

[a]*Department of Chemistry, Imperial College London, South Kensington, London SW7 2AZ, UK*
[b]*Department of Chemical Engineering, Imperial College, London, UK*

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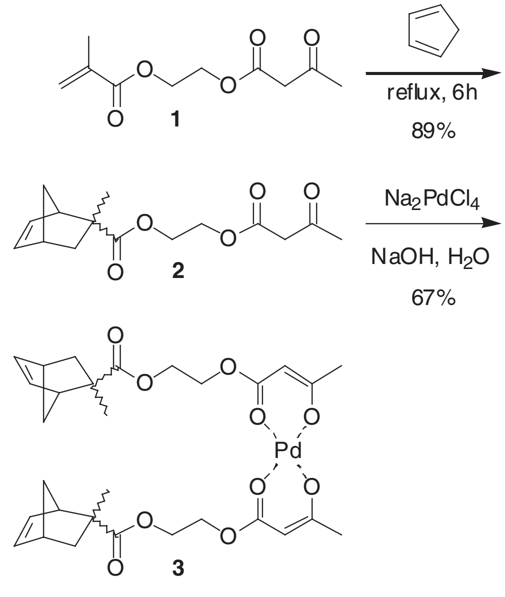
Abstract—Bis[1-(5-norbornen-2-yl)butan-1,3-dionato]palladium(II) was conveniently prepared from 5-acetoacetyl-2-norbornene and sodium tetrachloropalladate. The former could be subjected to ROMP to give a highly-loaded palladium(II) ROMP polymer with a palladium loading of 23% by weight.

Palladium(II) complexes are used extensively as powerful catalysts in organic transformations such as oxidation, C–C bond forming, allylic rearrangement, carbonylation, isomerisation and hydrogenation reactions.[1] On the other hand, immobilisation of metal complexes is a useful strategy to deliver catalysts that can be highly selective and at the same time easily recovered by phase separation. Immobilisation of palladium(II) complexes is relatively unexplored, however. The few reported examples include covalent heterogenisation of phosphine ligands over silica,[2] entrapment in zeolites[3] or encapsulation in mesoporous materials.[4] Mastrorilli and co-workers reported the radical co-polymerisation of an alkene in the side chain of a bis(ketoesterato)-palladium(II) complex with two co-monomers, to produce a polymeric material bearing Pd(II),[5] suitable for catalytic hydrogenation,[6] C–C bond-forming reactions[7] and allylic alkylation reactions.[8] A drawback of this approach, as a consequence of using co-monomers, is the low overall loading of the metal.

We now report a convenient method for the synthesis of polymeric materials with a high Pd(II) content via ring-opening metathesis polymerisation (ROMP) of Pd(II)-containing monomers.[9]



Scheme 1.

In order to achieve a palladium(II)-containing polymer via ROMP, we first elected to synthesise a β-ketoester (to ligate Pd(II) as a β-ketoesterate) with a pendant norbornene unit (for ROMPing). Accordingly, β-ketoester **2** was obtained as a 7:3 mixture of *exo* and *endo* isomers from the Diels–Alder reaction between cyclopentadiene and the commercially available

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* Corresponding author. E-mail: c.braddock@imperial.ac.uk

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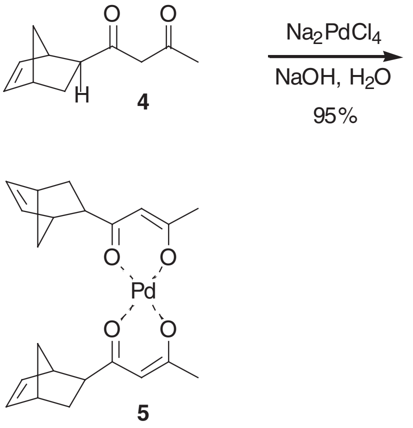
2-(methacryloyloxy)ethyl acetoacetate **1** (Scheme 1).[†] Complexation with palladium to give **3** was achieved by adding a solution of potassium or sodium chloropalladate in water to deprotonated ketoester **2**.[‡] On the basis of literature precedent,[10] this reaction yields the square-planar bis(ketoesterato)palladium(II) complex **3** as a mixture of *cis* and *trans* isomers about Pd. However, the situation is also complicated by the presence of the stereocentre in the norbornene unit such that each of the isomers at Pd can contain two *endo*, two *exo* or one *exo* and one *endo* norbornene units, further complicated by the fact that the norbornene is racemic (i.e., *R***R** or *R***S**) for a total of 14 diastereoisomers, and indeed, the ^{1}H NMR and ^{13}C NMR spectra proved to be extremely complex. Mass spectrometry confirmed the gross structure of complex **3** with a mass of 665 Da (M$^+$) and 385 Da (M ligand) with the distinctive isotope patterns for palladium. However, in some cases the formation of a compound with a mass of 989 Da with the distinctive isotope pattern for palladium was observed instead. A further problem was the tendency of this complex to 'oil out' of the preparative reaction mixture complicating its isolation, and its tendency to decompose in solution over several hours. Simplification was attempted by synthesis of the pure *exo* isomer of acetoacetate **2**, which was obtained from the esterification of *exo*-norbornene carboxylic acid and 2-hydroxyethyl acetoacetate. The *exo*-carboxylic acid was obtained from the Diels–Alder reaction of methacrylic acid and cyclopentadiene followed by the removal of the *endo*-isomer by iodolactonisation.[11] 2-Hydroxyethyl acetoacetate was synthesised from diketene and ethylene glycol in the presence of triethylamine.[12] Although this approach does simplify the resultant spectra, it was not possible to determine the structure of the heavier complex. Nevertheless, this material was carried through for ROMP studies (vide infra).



Scheme 2.

In a second approach to a convenient synthesis of a highly-loaded palladium(II) ROMP polymer, a norbornene-containing β-diketone (to instead ligate Pd(II) as a β-diketonate) was selected as the organic backbone for the monomer: the known *exo*-5-acetoacetyl-2-norbornene (**4**),[13§] was treated with aqueous base and sodium tetrachloropalladate as above to yield

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[†] *Synthesis of 2-(2-methylnorborn-5-ene-2-carboxylate)ethyl acetoacetate* (**2**). A mixture of α,β-unsaturated ester **1** (6.0 g, 28 mmol) and freshly cracked cyclopentadiene (3.7 g, 56 mmol) was refluxed for 6 h. The mixture was allowed to cool and the excess cyclopentadiene/dicyclopentadiene removed by reduced-pressure distillation and the residue chromatographed (EtOAc–petroleum ether; 60:40) to give the Diels–Alder adduct **2** (7.0 g, 89% yield) as a light yellow oil as a mixture of *endo* and *exo* isomers (ratio *endo*:*exo* = 3:7; this assignment was made on the basis of the preference for methacrylates to give the *exo* isomer as the predominant product in Diels–Alder reactions). The ^{1}H and ^{13}C NMR spectra of this mixture is further complicated by the presence of β-ketoester keto-enol tautomers (4:1; keto:enol) for each of the *endo* and *exo* isomers: IR (thin film, NaCl plates) 3061, 2974, 2876, 1722, 1656, 1633 cm^{-1}; δ_H (CDCl$_3$, 300 MHz) 11.82 (0.2H, s, enol OH), 6.20 (0.7H, m, *exo* alkene), 6.10 (0.3H, m, *endo* alkene), 6.06 (0.7H, m, *exo* alkene), 5.99 (0.3H, m, *endo* alkene), 4.98 (0.2H, s, enol C=C*H*), 4.40–4.20 (4H, m), 3.46 (1.6H, s), 2.99 (0.7H, s), 2.80–2.75 (1.3H, m), 2.39 (0.7H, dd, J = 12.1, 4.0 Hz), 2.26 (2.4H, s, keto CH$_3$), 1.94 (0.6H, s, enol CH$_3$), 1.90 (0.3H, dd, J = 12.1, 2.7 Hz), 1.53–1.20 (2H, m), 1.42 (0.9H, s, *endo* CH$_3$), 1.08 (2.1H, s, *exo* CH$_3$), 0.83 (1H, dd, J = 12.1, 2.7 Hz); δ_C (CDCl$_3$, 75 MHz) 200.1, 178.4, 177.1, 176.0, 172.2, 166.8, 138.7, 137.9, 135.2, 133.4, 89.4, 63.1, 62.2, 61.9, 61.6, 50.9, 50.3, 50.0, 49.8, 49.6, 49.0, 46.8, 42.8, 42.6, 37.9, 37.6, 30.1, 29.7, 26.3, 24.3, 21.2. Anal. Calcd for C$_{15}$H$_{20}$O$_5$: H, 7.19; C, 64.27. Found: H, 7.09; C, 64.35.

[‡] *Synthesis of bis[2-(2-methylnorborn-ene-2-carboxylate)ethyl acetoacetato]palladium(II)* (**3**). A solution of sodium tetrachloropalladate (92 mg, 0.31 mmol) was added to a solution of ketoester **2** (0.64 g, 2.28 mmol) and sodium hydroxide (91.2 mg, 2.28 mmol) in degassed water (9 mL). The mixture was extracted with CH$_2$Cl$_2$ (3 × 10 mL), and the combined organics were washed with water, evaporated under reduced pressure and dried under vacuum to give palladium(II) complex **3** (0.51 g, 68% yield) as an orange oil: IR (CDCl$_3$) 3064, 2975, 2877, 1720, 1602, 1513 cm^{-1}; MS (FAB$^+$) 663 (2.8%), 664 (5.3%) 665 (5.6%), 666 (3.6%), 667 (4.5%), 668 (1.7%), 669 (2.1%), 383 (5.6%), 384 (9.6%), 385 (13.4%), 386 (4.0%), 387 (9.9%), 388 (2.9%), 389 (5.9%).

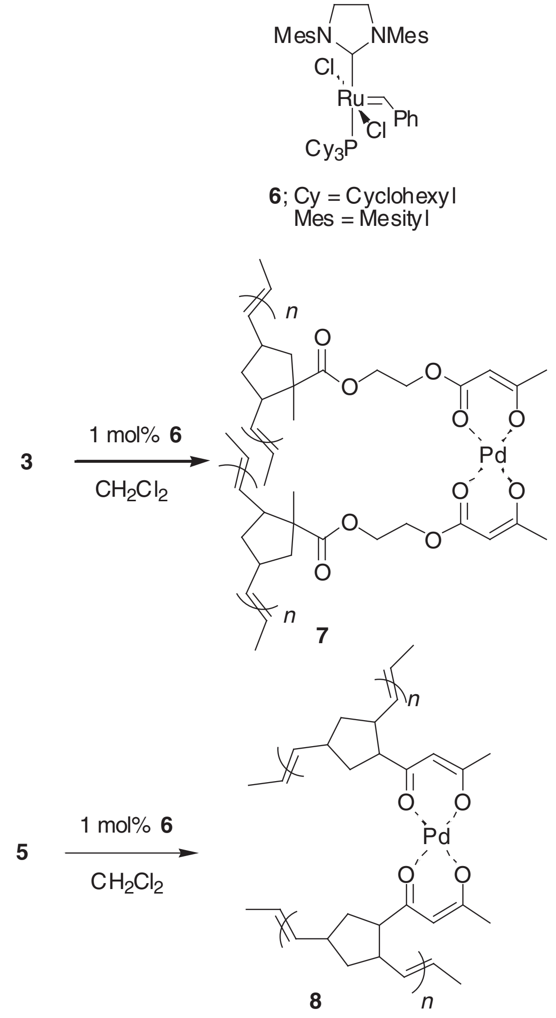
[§] *Synthesis of 5-acetoacetyl-2-norbornene* (**4**). 5-Acetyl-2-norbornene (4.0 g, 29.4 mmol, mixture of *endo* and *exo* isomers) was added to a suspension of sodium hydride (1.5 g, 62 mmol) in dry 1,2-dimethoxyethane (60 mL). Ethyl acetate (7.8 g, 88 mmol) was added and the mixture was refluxed for 16 h. The mixture was allowed to cool and quenched by pouring carefully into ice-cold HCl (35%, 12 mL). The organics were extracted with CH$_2$Cl$_2$, the combined organic layers were washed with saturated aqueous sodium chloride solution and saturated aqueous sodium bicarbonate solution, the solvent evaporated and the residue chromatographed (EtOAc–petroleum ether; 10:90) to give the *exo*-diketone **4** (1.33 g, 7.5 mmol, 30%) as a light yellow oil. The *exo* assignment was confirmed by oxidative cleavage[18] of diketone **4** to give *exo*-5-norbornene-2-carboxylic acid.[19] The diketone exists in a tautomeric equilibrium with its enol form (4:1; enol:keto): IR (thin film, NaCl plate) 3060, 2972, 2947, 2873, 1724, 1710, 1614 cm^{-1}; δ_H (CDCl$_3$, 300 MHz) >11 (0.8H, s, enol OH) (not observed), 6.14 (2H, br s, *H*C=C*H*), 5.57 (0.8H, s, 1H), 3.67 (0.4H, s, keto CH$_2$), 3.01–2.94 (2H, m), 2.43 (0.2H, m), 2.25 (0.6, s, keto CH$_3$), 2.19 (0.8H, m), 2.04 (2.4H, s, enol CH$_3$), 1.88 (1H, m), 1.54 (1H, m), 1.27 (2H, m); δ_C (CDCl$_3$, 75 MHz) 198.9, 188.5, 138.5, 138.2, 136.2, 135.6, 99.8, 57.9, 52.1, 47.3, 47.1, 46.3, 45.9, 45.2, 41.8, 30.9, 30.1, 29.0, 24.3; HRMS (EI$^+$) calcd for C$_{11}$H$_{14}$O$_2$ 178.0994, found 178.0993.

palladium(II) complex **5** (Scheme 2).[¶] In contrast to the handling and characterisation difficulties encountered with complex **3**, complex **5** was obtained as a yellow solid in essentially quantitative yield. This material was found to be stable on standing for at least one week and could be satisfactorily characterised by IR, ^{13}C NMR, MS and microanalysis.

Initial attempts to ROMP either monomer **3** or **5** with Grubbs' catalyst [(PCy$_3$)$_2$Cl$_2$RuCHPh; Cy = cyclohexyl][14] failed. However, using the more active *N*-heterocyclic carbene containing ruthenium benzylidene **6**,[15] ROMP proceeded smoothly to give the ROMP polymers **7** and **8**, respectively (Scheme 3).[‖] The resulting resins were initially orange but took on a brown colouration when dried. These ROMP resins were found to be insoluble in chlorinated, hydrocarbon and protic solvents. This may be attributed to the high degree of 'cross-linking' engendered by the Pd(II) centre.

Characterisation of the ROMP polymers was variously achieved by XPS, ICP and microanalysis. The binding energies derived from the XPS spectra of either polymer were consistent with the presence[16] of Pd(II), (Pd 3d$_{5/2}$, 3d$_{3/2}$; **7**: 336.9 and 342.2, **8**: 338.0 and 343.3). The overall Pd content was determined by ICP in the case of **7** and by elemental analysis for **8**. Using these methods the palladium content of the resins were found to be 6wt% (16wt% theoretical) and 23wt% (23wt% theoretical), respectively, the latter being a remarkably high overall Pd content.

In conclusion we have presented a method for the immobilisation of two *O*,*O*′-chelate palladium(II) complexes via ROMP. In particular, the bis(ketonato)palladium(II) complex **5** represents a readily synthesised monomer, which can be ROMPed under mild conditions, without the need for protection from the air or the use of specially dried solvents to give a highly-loaded (23% by weight) Pd(II)-containing polymer (**8**). The obtained materials should find use in catalytic applications with facile catalyst separation.[17]



Scheme 3.

Acknowledgements

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[¶] *Synthesis of bis[1-(5-norbornen-2-yl)butan-1,3-dionato]palladium(II)* (**5**). Following the procedure used for the preparation of sodium palladium(II) complex **3** from β-ketoester **2**, diketone **4** (2.67g, 15.0mmol) and sodium tetrachloropalladate (0.67g, 3.75mmol) gave palladium(II) complex **5** (1.7g, 7.1mmol, 95% yield) as a yellow solid. The ^{13}C NMR spectra indicates that the complex is an approximate 5:2 mixture of *cis* and *trans* isomers (not assigned) about Pd: mp 180°C (dec): IR (CDCl$_3$) 3062, 2978, 2873, 1549, 1510cm^{-1}; δ_C (CDCl$_3$, 75MHz) 192.8, 192.6, 186.7, 186.2, 138.2, 138.0, 136.4, 101.0, 100.5, 99.8, 48.1, 47.9, 47.4, 47.2, 46.6, 46.4, 46.3, 41.8, 31.3, 25.5; MS (FAB$^+$) 459 (3.7%), 460 (5.0%), 461 (6.9%), 462 (2.1%), 463 (4.8%), 464 (1.9%), 465 (2.6%), 281 (7.5%), 282 (12.0%), 283 (12.8%), 284 (5.0%), 285 (12.1%), 286 (3.3%), 287 (5.1%); Anal. Calcd for C$_{22}$H$_{26}$O$_4$Pd: H, 5.65; C, 57.34. Found: H, 5.75; C, 57.513.

[‖] *Procedure for ROMP of Pd(II) monomer complexes* **3** *and* **5**. The following procedure for the ROMP of complex **5** is representative: to a stirred solution of **5** (101mg, 0.22mmol) in CH$_2$Cl$_2$ (5mL) was added ruthenium benzylidene **6** (3.7mg, 1mol%). The mixture was stirred for 1h (polymer can be observed). Ethyl vinyl ether (10mL) was added to terminate the polymerisation and the mixture was stirred for 0.5h. The solid was isolated by filtration, washed with CH$_2$Cl$_2$ (3 × 50mL) and dried under vacuum to give ROMP polymer **8** (117mg, 116%) as a light-brown solid. Anal. Calcd for (C$_{22}$H$_{26}$O$_4$Pd)$_n$: H, 5.65; C, 57.34. Found: H, 5.76; C, 57.03.

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