Organometallics 1988, 7, 2261-2266

Preparation and Properties of Stacked Oligomeric and Polymeric Metallocenes

Regina Arnold, Stephen A. Matchett, and Myron Rosenblum*

Department of Chemistry, Brandeis University, Waltham, Massachusetts 02254

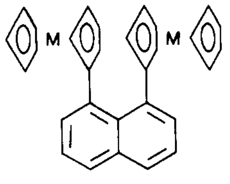
Received September 25, 1987

Zincated metallocenes, prepared from 1,1′-dilithioferrocene and 1,1′-dilithioruthenocene by treatment with anhydrous zinc chloride, have been coupled with 1,8-diiodonaphthalene in the presence of a palladium(0) catalyst. These reactions lead to oligomeric or low molecular weight polymeric metallocenes in which the separate metallocene units are held proximate and face-to-face by the bridging peri-substituted naphthalene rings.

Introduction

The past several years have seen an increasing interest in the synthesis and properties of stacked or columnar organometallic compounds. These systems comprise the multidecked nickelocenes[1] and related bifacial iron, cobalt, and nickel complexes of triboroles,[2] diboroles,[3] and thiadiborolenes,[3] and the phthalocyanine metal complexes joined through a covalent linkage[3,4] as well as the more recently reported paracyclophane ruthenium[6] and helicene iron complexes.[7] The generalized structural unit comprising a cyclopentadienyl ring bridging two π-bound metal atoms is also encountered in the crystal structures of $TlCp$,[8] $InCp$,[9] $(Me_5Cp)Sn^+$,[10] and thallium tricyanovinylcyclopentadienide[11] as well as in $PbCp_2$[12] and $CpZnMe$[13] in the solid state. The bonding and band structure of several of these compounds have recently been the subject of theoretical analyses.[14] In this paper we consider the preparation of a new type of stacked organometallic system based on cyclopentadienyl complexes, in which the individual metallocene units are held proximate and cofacial as peri substituents on a naphthalene ring.

We have previously described the synthesis of 1,8-diferrocenylnaphthalene[15] and 1,8-diruthenocenylnaphthalene[16] (**1a** and **1b**, respectively) through coupling of 1,8-diiodonaphthalene with metallocenylzinc chloride in the presence of palladium catalysts. The crystal structures and physical properties of these substances have also been reported.[15,16] The present report provides an account of the preparation and properties of oligomeric and polymeric materials based on the monomeric units **1a** and **1b**.



1a: M = Fe
b: M = Ru

Results and Discussion

We have found that palladium-catalyzed coupling of 1,1′-zincated metallocenes with 1,8-diiodonaphthalene affords either oligomeric or low molecular weight polymers based on **1** depending on reaction conditions. We had initially employed dichloro[1,1′-bis(diphenylphosphino)ferrocene]palladium[17] as catalyst in these reactions, but subsequent investigation has shown that dichloro-bis(triphenylphosphine)palladium is as effective. The active catalyst was generated in situ by reduction of the palladium(II) complex with DIBAL-H. The 1,1′-dimetalated metallocenes **2** were prepared by dilithiation of ferrocene or ruthenocene, employing butyllithium–TMEDA,[18] followed by treatment of the resulting dilithiometallocene with anhydrous zinc chloride. Initially, commercially available 1.0 M solutions of zinc chloride in ether were used to effect the conversion of lithiated metallocenes to the corresponding zinc reagents. However, under these conditions, we found it difficult to rigorously exclude adventitious moisture. This results in the conversion of dilithiometallocene, in part, to a monozincated metallocene and, consequently, to chain-terminating coupling reactions.[16] Indeed, when the molar ratio of zinc chloride to dilithiometallocene was 2:1, the major product of the palladium-catalyzed coupling reaction has been shown to be **1a** or **1b**. We have now found that when the ratio of these reactants is reduced to 1:1, the products from dilithioferrocene or ruthenocene are low molecular weight oligomers. The precise composition of zincated metallocene reagent in these reactions cannot be defined but is likely to be a mixture of dimetallocenylzinc as well as chlorozinc metallocenes. Furthermore, since zinc halide is formed continuously in the course of the coupling reaction, the composition of zincated metallocene in the reaction is likely to change continuously as well.

Oligomeric products from these reactions were initially purified on successive 1000-μm silica TLC plates, which

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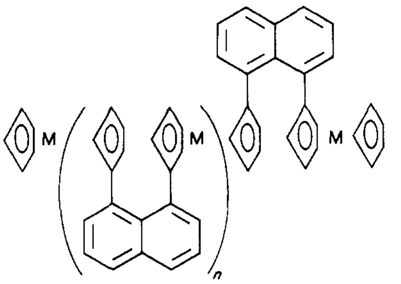
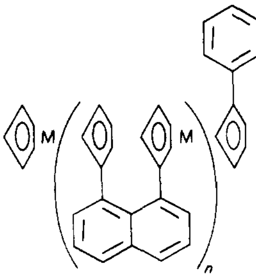
separated the product into a number of discrete bands. These were then subjected to HPLC analysis on a Waters 100-Å Ultrastyragel column. In general, complete separation of the reaction mixture into pure oligomeric products could not be achieved. The major and minor components in each fraction were characterized by field desorption or FAB mass spectrometry and by their proton NMR spectra. Mass spectra of all the products were characterized by a parent ion peak, with a well-defined isotope distribution pattern, which defines the number of metal centers present in the oligomer. This was especially true for ruthenocene oligomers, for which the isotope cluster is rich in detail, due to the existence of seven stable ruthenium isotopes.

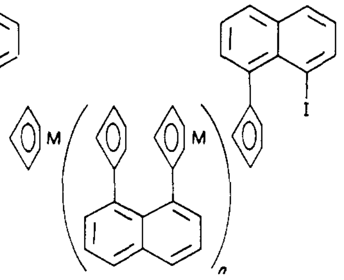
Analysis of the ferrocenylnaphthalene oligomeric mixture, which was separated into five bands on TLC, showed that the first fraction comprised principally the monomer **1a**. Material from the second band, isolated in trace amounts, consisted principally (70%) of the 2:2[19] oligomer **4a** (M = Fe) and a smaller amount (25%) of the closely related iodo 2:2 oligomer **5b** (M = Fe). The first of these minor products may derive from the second through metal halogen exchange, which is a common side reaction in this class of catalyzed coupling reactions, especially with the more reactive alkali-metal salts. Fraction 3 (1.2% yield) consisted almost entirely of the 2:3 oligomer **3a** (M = Fe), with a trace of the 3:4 oligomer **3b**. Fraction 4 (0.6%) was principally the 3:3 oligomer **4b** (M = Fe), containing the related iodo oligomer **5b** (M = Fe) and **3a**, while fraction 5 (1.4%) was principally the 3:4 oligomer **3b** (M = Fe). Material remaining in the TLC base line was further fractionated on silica plates and yielded the 4:5 oligomer **3c** (M = Fe, 1.3%).



3a: *n* = 1
b: *n* = 2
c: *n* = 3
d: *n* = 4
e: *n* = 5



4a: *n* = 1
b: *n* = 2
c: *n* = 5
d: *n* = 6



5a: *n* = 1
b: *n* = 2

The same reaction, carried out with 1,1′-dilithioruthenocene, gave a very similar distribution of oligomeric products, except that the yields of these were significantly higher and in addition the homologous 5:6 oligomer **3d** (M = Ru) could be isolated in 2% yield. The mass spectrum of this latter substance, which is shown in Figure 1, reveals the presence of a small amount of the next higher homologue, the 6:7 oligomer **3e** at *m/e* 2365, as well as the 6:6 oligomer **4c** at *m/e* 2133 and a trace of the 7:7 oligomer **4d** at *m/e* 2490. Figure 2 shows the isotope distribution pattern for the molecular ion corresponding to the 5:6 oligomer **3d**. The complex envelope is a distinctive characteristic of these polyruthenium compounds and effectively identifies the composition of the molecular ion, through a comparison of the calculated and observed distribution of isotopic peaks.

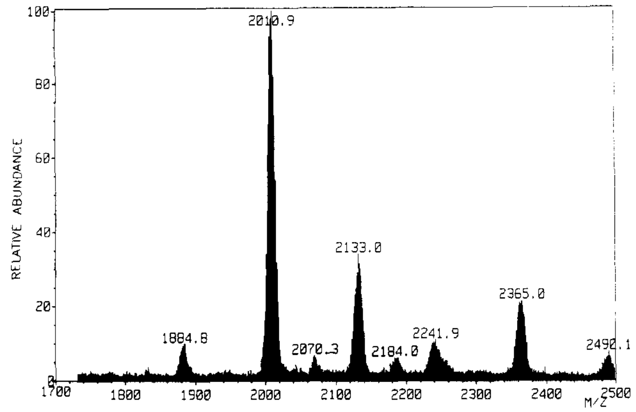


Figure 1. FD spectrum of ruthenocene oligomer **3d** (*m/e* 2011), with smaller amounts of oligomers **4c** (*m/e* 2133) and **3e** (*m/e* 2365), and a trace of **4d** (*m/e* 2490).

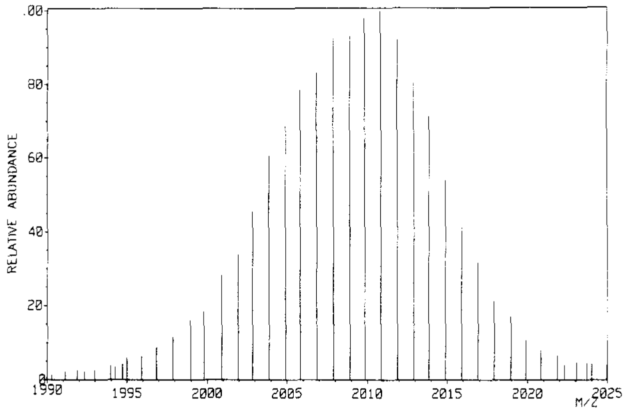
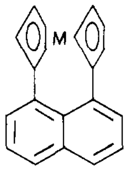


Figure 2. Observed distribution of isotope peaks for the parent cluster $C_{110}H_{80}Ru_6$ (**3d**).

In none of these reactions was any of the product of intramolecular coupling, **6**, isolated.[20] Processes leading to the formation of such a structure could in principle compete with the chain initiation step, but possibly owing to stereochemical constraints, such intramolecular coupling of the intermediate iodoferrocenylnaphthalene does not compete with the cross-condensation reaction.



6

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[19] The numbers used in this shorthand descriptor of structure represent the numbers of naphthalene and metallocene units, respectively, in the oligomer.

[20] The iron complex **6** has recently been prepared in our laboratories by an independent route.

Table I. ^{1}H NMR Spectral Data (δ) for Ruthenocene Oligomers

	Cp proton resonances		
compd	α-protons	unsubstitd Cp ring	β-protons
1b	4.66	4.36	4.33
3a	4.59, 4.46	4.33	4.27, 4.12
3b	4.58, 4.42, 4.40	4.32	4.25, 4.10, 4.07
3c	4.58, 4.42, 4.38, 4.36	4.31	4.25, 4.09, 4.06, 4.04
3d	4.58, 4.41, 4.38, 4.355, 4.35	4.31	4.25, 4.08, 4.06, 4.035, 4.03

Among those processes leading to chain termination, the presence of trace amounts of water or residual hydroxyl groups in the zinc chloride reagent is likely to be a principal contributor. The isolation of oligomers such as **4a–d** in which an iodo group has been lost from the naphthalene unit suggests that metal halogen exchange in the oligomer may also compete with chain growth. However, this process is evidently a minor reaction path, in both the iron and ruthenium reactions, since these latter products are very small components of the reaction mixture.

NMR Spectra. While the proton NMR spectra of ferrocene-based oligomers are not highly diagnostic of oligomer structure, those of the ruthenocene series are, in that they show separate or only partially overlapping triplets for each of the α- ($H_{2,5}$) and β- ($H_{3,4}$) cyclopentadienyl ring protons on each of the structurally distinct ruthenocene units. Thus, oligomers **3a–d** (M = Ru) show two sets of two, three, four, and five triplet resonances, respectively between δ 4.0–4.30 and δ 4.35–4.6 for α- and β-cyclopentadienyl protons on structurally distinct cyclopentadienyl rings (Table I). The low field set of triplets are assigned to α-protons on the substituted cyclopentadienyl rings and the high field set to β-protons on these rings, in conformity with the general observation that protons α to the substituent in arylated ferrocenes are generally more deshielded than are β-ring protons.[21] As the chain length of the oligomer increases, α- and β-ring protons on those cyclopentadienyl rings that are nearer to the structural center of the oligomer give rise to resonances at increasingly higher field. Those further toward the periphery of the chain also show increased shielding, as do protons on the terminal, unsubstituted cyclopentadienyl ring, compared with their lower molecular weight analogues.

Finally, the presence of a *single* resonance signal for α- ($H_{2,5}$) and β- ($H_{3,4}$) protons on each of the structurally distinct cyclopentadienyl rings requires that, as in the monomer, the chain must be capable of undergoing a rapid rotational flexing motion, which exchanges pairs of diastereotopic hydrogens in all of the cofacial cyclopentadienyl rings. This can only occur through rotation of these rings past one another, concerted with exchange of out-of-plane distortions in the naphthalene ring.[15] Such flexing would have to occur concertedly throughout the oligomeric chain, since the monomeric units are rigidly linked to one another.

Electrochemistry. The effect of increasing chain length on the oxidation potential of the metal centers was examined by cyclic voltammetry. Half-wave potentials, determined from peak potentials, are recorded in Table II for **1a**, **3a**, and **3b** (M = Fe),[22] and for α-naphthylferrocene. All of the redox reactions showed good chemical reversibility, but $E_{pa} - E_{pc}$ values were generally in the range of 100–200 mV under the conditions of measurement in methylene chloride. Compound **3b**, notwithstanding the presence of four oxidizable metal centers, showed only three distinct waves at a scan rate of 100 mV/s. At lower scan rates, the redox reaction becomes irreversible, with the appearance of a strong cathodic wave at 0.466 V, suggestive of an ECE process. A comparison of half-wave potentials for the iron compounds shows a progressive decrease in the first and second oxidation potentials with growth of the chain length, but this change diminishes sharply with increasing chain length. Furthermore, the difference in half-wave potentials for successive oxidation steps within a particular compound also shows a progressive diminution in comparing the data for **1a**, **3a**, and **3b**. Both of these effects reflect some degree of electronic interaction and charge delocalization between the metal centers of the partially oxidized species in the growing chain, either by direct interaction of the cofacial π-orbitals or metallocene units or by electronic relay through the naphthalene nuclei.

Table II. Half-Wave Potentials for α-Naphthylferrocene and Related Oligomers[a]

compd	E1/2 (1)	E1/2 (2)	E1/2 (3)
α-naphthylferrocene	0.548		
1a	0.389	0.597	
3a	0.296	0.461	0.592
3b	0.285	0.401	0.561

[a] Measurements were carried out by using 0.1 M tetra-*N*-butylammonium perchlorate in methylene chloride as supporting electrolyte, at a scan rate of 50 mV s^{-1}, and are referenced to SCE.

Polymers. In order to more effectively carry out the conversion of dilithioferrocene to the corresponding zinc derivative and thus foreclose chain-terminating processes, it was necessary to remove traces of water or hydroxyl end groups in the "anhydrous" zinc chloride reagent. We found that this could be accomplished by treating the salt with oxalyl chloride either under reflux conditions or on prolonged standing at room temperature.[23] When the palladium coupling reaction was carried out with the zincated ferrocene reagent prepared from freshly treated zinc chloride, low molecular weight polymeric material was formed, which precipitates from solution during the reaction. The reaction products were separated into an ether-soluble fraction, which contained principally **1a** and oligomers through the 3:4 oligomer **3b**, a second fraction, readily soluble in benzene, which contains the 3:4 and 4:5 oligomers **3b** and **3c**, respectively, and low molecular weight polymers, and a final fraction, obtained by Soxhlet extraction of the residual orange solid with benzene. Molecular weight determinations carried out on these latter two samples by gel permeation chromatography[24] gave values of M_w and M_n of 1600 and 940, respectively, for the second fraction and of 6000 and 3600, respectively, for the third fraction. A plot of molecular weight and

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(21) Rosenblum, M. *Chemistry of The Iron Group Metallocenes*; Interscience: New York, 1965; p 215.

(22) No attempt was made to determine oxidation potentials for the ruthenium compounds, since the electrochemistry of ruthenocene, in contrast to that of ferrocene, is known to be complex. For a recent summary, see: Seddon, E. A., Seddon, K. R. *The chemistry of Ruthenium*; Elsevier: Masterdam, 1984; p 750.

(23) We are indebted to Professor J. R. Norton for suggesting the use of an acid chloride drying reagent for removing residual hydroxyl groups in the zinc chloride.

(24) Grubisic, A.; Rempp, P.; Benoit, H. *J. Polym. Sci., Polym. Lett. Ed.* **1967**, *5*, 753.

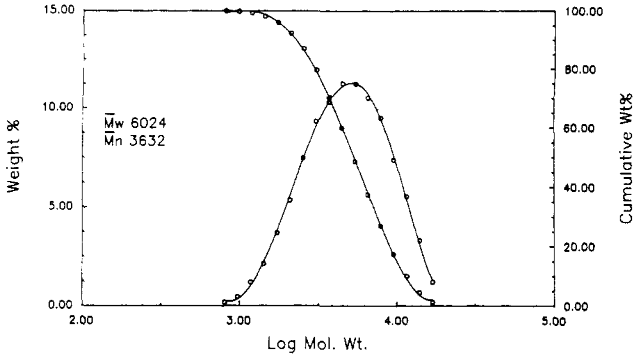

Figure 3. Molecular weight and cumulative molecular weight distribution in ferrocene polymer.

cumulative weight distribution for this latter material is given in Figure 3, which shows the presence of a small but significant amount of polymeric material with molecular weights in the range of 15000–18000. Both of the polymer fractions show a heightened sensitivity to air oxidation compared with the lower molecular weight oligomeric ferrocenes, indicative of a further decrease in oxidation potential for the metallocene nuclei in the polymer. These oxidized materials precipitate progressively from benzene solutions of the polymers on exposure to air and, unlike the lower molecular weight oligomers **3a–c**, are only partially resolubilized on treatment with bisulfite.

Conclusion

Palladium-catalyzed cross coupling has been shown to be an effective means for the preparation of oligomeric and polymeric metallocenes based on a 1,8-dimetallocenylnaphthalene monomer. The substances obtained in these reactions constitute unique molecular chains of stacked face-to-face metallocenes with bridging, peri-disubstituted naphthalene spacing units. The preparation of higher molecular weight materials and the study of their chemical and physical properties as well as the application of this chemistry to other metallocenes are in progress.

Experimental Section

All reactions were carried out under an atmosphere of dry nitrogen or argon. Air and/or moisture-sensitive reagents were handled by using standard syringe transfer techniques and flasks capped with rubber septa. Flexible double-tipped needles (cannulas) were used to transfer large amounts (> 10 mL) of liquid or reagents. Solvents were dried by standard procedures and stored under nitrogen. Tetrahydrofuran was freshly distilled from sodium benzophenone ketyl prior to use.

Reactions were monitored by thin-layer chromatography on silica gel slides and by gel permeation chromatography on a 100-Å Ultrastyragel column Waters) with THF as eluent at a flow rate of 1 mL/min. Preparative plates (Analtech Silica Gel GF, 1000 microns) were used to isolate products.

Ruthenocene (Polysciences), *N,N,N′,N′*-tetramethylethylenediamine (TMEDA, Aldrich), and diisobutylaluminum hydride (DIBAL-H, Aldrich) were used as purchased. Butyllithium (2.5 M solution in hexanes, Aldrich) was assayed by titration with 2-butanol and 2,2′-dipyridyl or with 1,3-diphenylacetone *p*-tosylhydrazone as indicator. Anhydrous zinc chloride (Alfa, ultrapure) or a 1.0 M solution in diethyl ether (Alfa) was used. 1,8-Diiodonaphthalene was prepared as described in the literature.[25]

NMR spectra were recorded on a Varian XL300 spectrometer (NIH-1-S10RR01493-01-A1) and referenced to solvent $CHCl_3$.

Mass spectra were recorded at the MIT mas spectrometry laboratory on a Varian MAT 731 high-resolution mass spectrometer with a combined EI/FI/FD ion source and FAB gun or on a JEOL HX110/HX110 spectrometer. For **3d** (M = Ru), FD spectra were obtained for a methylene chloride solution of the sample, applied to a silicon emitter, using a microsyringe. The mass scale calibration was made by using CsI clusters and should be accurate within 0.2 μm.

Electrochemical measurements were carried out under an argon atmosphere in methylene chloride which had been distilled from anhydrous P_2O_5 under a nitrogen atmosphere. Cyclic voltammograms were obtained by using a Princeton Applied Research Model 173 potentiostat–galvanostat, a Model 176 current to voltage converter, and a Model 175 universal programmer. Data were recorded on a Bascom-Turner Model 3120T digital recorder at a digitization rate sufficient to record data points at 2-mV intervals or less. Potentials reported are at a Pt disk electrode and are reported vs a saturated calomel electrode at a scan rate of 50 mV s^{-1}.

Polymer molecular weights were determined by using a Polymer Laboratory PLgel 500 +10E4, 30 cm × 7.8 mm column at 30 °C with toluene at 1 mL/min. Detectors were a Viscotek Model 100 differential viscometer and a Waters R401 differential refractometer in series at 30 °C. Calibration was carried out by using polystyrene standards.

Elemental analyses were performed by E and R Microanalytical Laboratory, Inc., Corona, NY.

Preparation of Ferrocenylnaphthalene Oligomers. A 100-mL Schlenk flask was charged with 3.43 g (18.44 mmol) of ferrocene as a suspension in 25 mL of distilled hexane. This suspension was lithiated with 2 equiv (36.88 mmol) of *n*-butyllithium over the course of 15 min. The suspension was then treated with 2 equiv (36.88 mmol) of TMEDA and allowed to stir at room temperature overnight. The pale orange powdered product (dilithioferrocene–$^2/_3$-*N,N,N′,N′*-tetramethylethylenediamine) was isolated via cannula filtration and dried under vacuum to yield 4.563 g of product (87%), which was stored in a drybox. This was used as a stock for subsequent coupling reactions.

In a typical preparation, 0.382 g (1.38 mmol) of the dilithioferrocene complex was dissolved in 20 mL of distilled THF. This orange solution was cooled to 0 °C and treated with 1 molar equiv of $ZnCl_2$ (1.38 mL of a 1 M solution in ether). This was allowed to stir at 0 °C for 0.5 h.

The Pd catalyst was prepared *in situ* in a round-bottom flask fitted with a reflux condenser that was capped by a side-arm Schlenk adaptor. The catalyst was prepared by reducing 0.048 g (5 mol %) of $(PPh_3)_2PdCl_2$ with 2 equiv of DIBAL-H in 2 mL of THF, yielding a black solution. The ferrocenyl zinc complex was then transferred via cannula into the catalyst solution, yielding a brown suspension. This suspension was brought to reflux.

A solution of 0.524 g (1.38 mmol) of diiodonaphthalene in 5 mL of distilled THF was added dropwise down the reflux condenser over the course of 7.5 h. The progress of the reaction was monitored by gel permeation HPLC (Waters 100-Å Ultrastyragel column, THF, 1 mL/min). The reaction mixture was allowed to reflux for one additional hour after the addition was complete at which point the HPLC showed no additional changes in the product mixture.

The reaction was hydrolyzed by pouring the solution into 50 mL of saturated sodium chloride solution. Additional THF (20 mL) was added. The THF layer was removed and evaporated to dryness. The residue was then dissolved in CH_2Cl_2, dried over $MgSO_4$, filtered, and evaporated to yield the crude product as a dark orange-red oily solid.

The crude product was dissolved in 12 mL of CH_2Cl_2 and separated by preparative TLC (8:2 hexane/CH_2Cl_2, required 12 plates). The first few bands (not orange) on each plate were discarded having been demonstrated by ^1H NMR to contain no cross-coupled products. The remaining five bands and the base line were isolated from each plate, extracted into CH_2Cl_2, and evaporated to dryness to yield orange solids.

Of those isolated, band one gave the previously characterized 1,8-diferrocenylnaphthalene. This was 85% pure by HPLC (V_r = 7.75 mL), containing an uncharacterized impurity of higher molecular weight (V_r = 6.77 mL). This impurity could not be removed by chromatography on silica under a variety of conditions.

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(25) House, H. O.; Koepsell, D. G.; Campbell, W. J. *J. Org. Chem.* **1972**, *37*, 1003.

The second band was isolated in trace amounts and identified as the 2:2 oligomer **4a**. This oligomer was 70% pure by HPLC (R_{vol} = 7.23 mL), again containing an inseparable impurity with V_r = 6.46 mL. **4a**: ^{1}H NMR ($CDCl_3$) δ 8.3–6.9 (overlapping mult, 13 H), 4.27 (t, J = 1.8 Hz, 2 H), 4.23 (t, J = 1.8 Hz, 1 H), 4.08 (t, J = 1.8 Hz, 2 H) 4.06 (t, J = 1.8 Hz, 2 H), 3.96 (t, J = 1.8 Hz, 1 H), 3.85 (t, J = 1.8 Hz, 1 H), 3.82 (s, 5 H), 3.80 (t, J = 1.8 Hz, 2 H), 3.76 (t, J = 1.8 Hz, 1 H); MS (FD), m/e 622.

Band three contained 0.019 g (1.2%) of the 2:3 oligomer **3a** (71% pure by HPLC, R_{vol} = 6.86 mL), with an impurity at V_r = 6.22 mL: ^{1}H NMR ($CDCl_3$) δ 8.0 (d, J = 7.5 Hz, 2 H), 7.68 (d, J = 7 Hz, 2 H), 7.62 (mult, 4 H), 7.40 (t, J = 7 Hz, 2 H), 7.06 (t, J = 7 Hz, 2 H), 3.99 (br s, 4 H), 3.78 (s, 10 H), 3.74 (br s, 4 H), 3.50 (br s, 4 H); MS (FD), m/e 806.

Band four gave 0.0082 g (0.6%) of the 3:3 oligomer **4b** (94% pure by HPLC, V_r = 6.53 mL): ^{1}H NMR ($CDCl_3$) δ 8.3–6.9 (overlapping mult, 19 H), 4.21 (t, J = 1.8 Hz, 1 H), 4.03 (t, J = 1.8 Hz, 1 H), 3.77 (s, 5 H), 3.73 (br mult, 10 H), 3.39 (br s, 4 H); MS (FD), m/e 932.

Band five yielded 0.022 g (1.4%) of the 3:4 oligomer **3b** (pure by HPLC except for small shoulder, V_r = 6.28 mL): ^{1}H NMR ($CDCl_3$) δ 7.98 (d, J = 7 Hz, 2 H), 7.67 (d, J = 7 Hz, 2 H), 7.58 (mult, 6 H), 7.38 (t, J = 7 Hz, 2 H), 7.00 (mult, 6 H), 3.97 (br s, 4 H), 3.77 (s, 10 H), 3.68 (br mult, 12 H), 3.45 (br mult, 8 H); MS (FD), m/e = 1116.

The base lines of all the prep TLC paltes were isolated, extracted into CH_2Cl_2, filtered, and evaporated to dryness. The dark orange residue was redissolved in 3 mL of CH_2Cl_2 and separated by preparative TLC (5 × 1000 micron silica plates, 6:4 hexane/CH_2Cl_2). The chromatography gave predominantly one band, which was centered between two very weak bands. This center band was isolated to give 0.026 g of a dark orange solid. The HPLC showed predominantly one peak at V_r = 5.92 mL (1.3%). Slow recrystallization at −30 °C from CH_2Cl_2/Et_2O gave 0.005 g of the 4:5 oligomer **3c** as a microcrystalline material: ^{1}H NMR ($CDCl_3$) δ 7.98–6.99 (overlapping mult, 24 H), 3.97 (br s, 4 H), 3.78 (s, 10 H), 3.72 (br s, 4 H), 3.68 (br s, 4 H), 3.60 (br s, 4 H), 3.53 (br s, 4 H), 3.45 (br s, 4 H), 3.39 (br s, 4 H), 3.32 (br s, 4 H); MS (FD), m/e 1426 (FAB), 1427.

Preparation of Ruthenocenylnaphthalene Oligomers. To a suspension of ruthenocene (0.470 g, 2.03 mmol) in 18 mL of hexane was added via syringe 2.7 mL (4.06 mmol) of *n*-butyllithium (1.5 M in hexanes) followed by TMEDA (0.61 mL, 4.06 mmol). After being stirred overnight at room temperature, the flask, which now contained a suspension of 1,1′-dilithioruthenocene–TMEDA, was cooled to 0 °C, the supernatant was removed by cannula filtration, and the residual pale yellow solid was dissolved in 10 mL of THF. The supernatant was hydrolyzed with 1 N HCl, and the hexane layer was dried over Na_2SO_4 and evaporated to give 64 mg (14%) of recovered ruthenocene. Thus 406 mg (1.76 mmol) was converted to the dilithio–TMEDA complex. Exactly 1 molar equiv of zinc chloride (1.76 mL of a 1 M solution in ether) was added dropwise at 0 °C. A flocculent precipitate formed and persisted upon warming to room temperature. The pale yellow Zn-reagent suspension was stirred for 3 h and was then transferred by cannula to an addition funnel on top of a three-neck flask charged with the catalyst, prepared in situ from $(Ph_3P)_2PdCl_2$ (55 mg) and DIBAL-H (0.17 mL of a 20 wt % solution in toluene) in 2 mL of THF. A solution of 1,8-diiodonaphthalene (0.679 g, 1.78 mmol) in 5 mL of THF was added to this. The Zn reagent was added to this flask in portions over 30 min at 0 °C. The reaction mixture, a light brown suspension, was allowed to come to room temperature and stirred overnight whereupon it became homogeneous. The progress of the oligomerization was monitored by HPLC. Samples were prepared by passing an aliquot through a Sep-Pak silica cartridge with THF as the eluent. The resulting solution was diluted as needed and filtered (0.45-μm filter units) before injection. The consumption of diiodonaphthalene was slow at room temperature. However, traces of oligomers with molecular weights greater than the 2:3 oligomer **3a** were already detectable. Upon heating to reflux the size and relative amounts of oligomers increased with a concomitant decrease in diiodonaphthalene. Refluxing was continued until the HPLC profile remained constant (28 h). The reaction mixture was hydrolyzed with 1 N HCl at 0 °C. Evaporation of the organic layer gave a brown two-phase (oil–water) residue which was taken up in CH_2Cl_2, washed with water, and dried over $MgSO_4$. The crude product, an amber semicrystalline syrup, was separated by preparative TLC using hexane–methylene chloride (4:3) as eluent. Nine plates were required for separation of the product into eight fractions. Fraction one gave 200 mg of diiodonaphthalene. The products from the other fractions were further purified by flash chromatography through an 18-cm column of neutral alumina (Brockman grade III) with hexane–methylene chloride (1:1) to remove trace impurities. The oligomers, isolated in this way, were pale yellow solids. The yields reported are based on diiodonaphthalene consumed.

Band two gave 123 mg (16.6%) of 1,8-diruthenocenylnaphthalene, **1b** (73% pure by HPLC, V_r = 7.84 mL), containing the 2:2 oligomer **4a** (M = Ru): ^{1}H NMR ($CDCl_3$) δ 4.33 (t, J = 1.8 Hz, 4 H), 4.36 (s, 10 H), 4.66 (t, J = 1.8 Hz, 4 H), 7.28 (t, 2 H), 7.67 (d, 2 H), 7.87 (d, 2 H).

Band three gave 74 mg (12.5%) of the 2:3 oligomer **3a** (M = Ru) (V_r = 6.91) with a trace of the iodo oligomer **5b** (M = Ru): MS (FAB), m/e 1193 ($C_{60}H_{43}Ru_3I$). **3a**: ^{1}H NMR ($CDCl_3$) δ 4.12 (t, J = 1.8 Hz, 4 H), 4.27 (t, J = 1.8 Hz, 4 H), 4.33 (s, 10 H), 4.46 (t, J = 1.8 Hz, 4 H), 4.59 (t, J = 1.7 Hz, 4 H), 6.98 (t, 2 H), 7.26 (t, 2 H), 7.58 (2 overlapping d's, 4 H), 7.64 (d, 2 H), 7.81 (d, 2 H); MS (FAB), m/e 943 ($C_{50}H_{38}Ru_3$).

Band four gave 33 mg (5.9%) of the 3:4 oligomer **3b** (M = Ru) (V_r = 6.31 mL), pure by HPLC: ^{1}H NMR ($CDCl_3$) δ 4.07 (t, J = 1.5 Hz, 4 H), 4.10 (t, J = 1.8 Hz, 4 H), 4.25 (t, J = 1.5 Hz, 4 H), 4.32 (s, 10 H), 4.40 (t, J = 1.8 Hz, 4 H), 4.42 (t, J = 1.7 Hz, 4 H), 4.58 (t, J = 1.5 Hz, 4 H), 6.94 (t, 2 H), 6.95 (t, 2 H), 7.24 (t, 2 H), 7.55 (overlapping d's, ~8 H), 7.63 (d, 2 H), 7.80 (d, 2 H). MS (FAB), m/e 1298 ($C_{70}H_{52}Ru_4$). Anal. Calcd for $C_{70}H_{52}Ru_4$: C, 64.80; H, 4.04. Found: C, 60.44; H, 4.07.

Band five gave 19 mg (2.7%) of the 4:5 oligomer **3c** (M = Ru) (V_r = 5.91 mL), pure by HPLC: ^{1}H NMR ($CDCl_3$) δ 4.04 (t, J = 1.8 Hz, 4 H), 4.06 (t, J = 1.5 Hz, 4 H), 4.09 (t, J = 1.5 Hz, 4 H), 4.25 (t, J = 1.8 Hz, 4 H), 4.31 (s, 10 H), 4.36 (t, J = 1.8 Hz, 4 H), 4.38 (t, J = 1.8 Hz, 4 H), 4.42 (t, J = 1.8 Hz, 4 H), 4.58 (t, J = 1.8 Hz, 4 H), 6.92 (t, 2 H), 6.93 (t, 2 H), 6.94 (t, 2 H), 7.24 (t, 2 H), 7.52 (m, ~12 H), 7.62 (d, 2 H), 7.80 (d, 2 H). Anal. Calcd for $C_{90}H_{66}Ru_5$: C, 65.40; H, 4.03. Found: C, 64.61; H, 4.39.

Band six gave 10 mg (2%) of the 5:6 oligomer **3d** (M = Ru) (V_r = 5.57 mL), pure by HPLC: ^{1}H NMR ($CDCl_3$) δ 4.030, 4.035 (two overlapping t's, 8 H), 4.06 (t, J = 1.5 Hz, 4 H), 4.08 (t, J = 1.5 Hz, 4 H), 4.25 (t, J = 1.8 Hz, 4 H), 4.31 (s, 10 H), 4.350, 4.355 (2 overlapping t's, 8 H), 4.38 (t, J = 1.8 Hz, 4 H), 4.41 (t, J = 1.8 Hz, 4 H), 4.58 (t, J = 1.8 Hz, 4 H), 6.92 (m, ~8 H), 7.24 (t, 2 H), 7.52 (m, 16 H), 7.62 (d, 2 H), 7.80 (d, 2 H); MS (FAB), m/e 2010.9 ($C_{110}H_{80}Ru_6$).

Synthesis of Ferrocene Polymers. A Schlenk flask was loaded with 0.191 g (1.4 mmol) of finely ground $ZnCl_2$. Into this flask was condensed 3–5 mL of oxalyl chloride by bulb to bulb vacuum transfer. This helps to remove discoloring impurities from the oxalyl chloride. The resulting suspension was placed under argon and then brought to reflux for 2 h, then allowed to cool to room temperature, and stirred under argon for an additional 2 h. The oxalyl chloride was then removed in vacuo to yield a cream solid that was left under dynamic vacuum for 1 h to remove volatiles (alternatively, the suspension of zinc chloride in oxalyl chloride may be stirred for 1–2 days under argon, resulting in somewhat less discoloration of the $ZnCl_2$ and comparable reactivity). The reagent was then dissolved in 8 mL of THF to give a clear solution.

Following the standard procedure previously outlined, 0.260 g (1.4 mmol) of ferrocene was dilithiated with *n*-butyllithium (2.8 mmol) in the presence of TMEDA (0.42 mL, 2.8 mmol). The resulting light orange solid was dissolved in 10 mL of THF, yielding a dark orange solution. This solution was treated with the $ZnCl_2$ solution via cannula transfer and allowed to stir 1 h prior to use. The resulting reagent was an orange suspension. The reagent was transferred to a three-neck, 100-mL flask fitted with a stopper, a reflux condenser, and an addition funnel.

The Pd(0) catalyst was prepared in a separate flask by reducing 0.049 g (0.07 mmol, 5 mol % based on ferrocene) with 2 equiv of DIBAL-H (0.14 mmol, 0.14 mL of a 1.0 M solution in toluene) in 2 mL of THF. The black solution of Pd(0) was transferred into the flask containing the ferrocenylzinc reagent, and the resulting suspension was brought to reflux.

Table III. Summary of Retention Volumes in Toluene for the Ferrocene Oligomers[a]

oligomer	retentn vol (mL)
1:8 diferrocenylnaphthalene (**1a**)	18.36
2:2 oligomer (**4a**)	17.84
2:3 oligomer (**3a**)	16.72
3:3 oligomer (**4b**)	16.40
3:4 oligomer (**3b**)	14.15
4:5 oligomer (**3c**)	13.80

[a] 500- and 100-Å Ultrastyragel columns in series, using toluene at 1 mL/min.

As the solution began to reflux, 0.532 g of 1,8-diiodonaphthalene as a solution in 10 mL of THF was slowly dripped into the reaction over the course of 5 h.

When the addition was complete, the reaction was allowed to continue refluxing with periodic monitoring by gel permeation HPLC (500- and 100-Å Ultrastyragel columns linked in series, THF at 1.0 mL/min). After only 3 h the reaction had produced a molecular weight distribution typical of the 3:4 and 4:5 range of oligomers. Typically, the 1,8 diferrocenylnaphthalene dominated these reactions, but here it was seen in only small amounts. At this point, black particles in the solution suggested decomposition of the Pd(0) catalyst and another 5 mol was added.

After 12 h a large amount of orange precipitate had formed. Its lower solubility in THF made characterization of the product distribution by HPLC unreliable in this solvent. The reaction was run for a total of 36 h at reflux and then worked up as described for the other syntheses.

Attempts to separate the oligomers by column chromatography gave poor resolution due to the wide range of molecular weights and the low solubility of the higher oligomers in solvent combinations which resolve the lower molecular weight species. The product distribution was therefore fractionated in the following series of extractions. In order to compare the fractions to the characterized oligomers, the gel permeation chromatography was performed in toluene which readily solubilized all of the fractions (500- and 100-Å Ultrastyragel columns in series, toluene at 1.0 mL/min). A table of retention volumes in toluene for the known oligomers appears in Table III for comparison.

Extracting the crude product with diethyl ether gave the first fraction which contained all of the lower molecular weight oligomers (1,8-diferrocenylnaphthalene through the 3:4 oligomer), as confirmed by the distribution of the retention volumes in the HPLC. This material weighed 77 mg, or approximately 17% of theoretical product yield.

The remaining solid was then washed with benzene to give the second fraction (56 mg). This fraction contained a small amount of oligomer in the 3:4 and 4:5 range. Molecular weight determination of this fraction gave M_w = 1600 and M_n = 940.

The third and final fraction was collected by Soxhlet extraction of the remaining solids in benzene to give 55 mg of product as a dark red powder. A molecular weight determination carried out on this material gave M_w = 6000 and M_n = 3600.

Acknowledgment. This research was supported by a grant from the Department of Energy (85Er45193) which is gratefully acknowledged. The investigation was supported (in part) by the National Institutes of Health Research Grant No. RR00317 from the Biotechnology Resources Branch, Division of Research Resources (Principal Investigator: Professor K. Biemann). We are grately indebted to Dr. Stanley Clark, Research Division, Polaroid Corp., for carrying out the determination of molecular weights of ferrocenyl polymers.

Registry No. **1a**, 94161-70-3; **1b**, 112461-16-2; **3a** (M = F), 113792-95-3; **3a** (M = Ru), 113792-98-6; **3b** (M = Fe), 113792-96-4; **3b** (M = Ru), 113793-00-3; **3c** (M = Fe), 113792-97-5; **3c** (M = Ru), 113793-01-4; **3d** (M = Ru), 113830-86-7; **56** (M = Ru), 113792-99-7; $(PPh_3)_2PdCl_2$, 13965-03-2; ferrocene, 102-54-5; dilithioferrocene, 33272-09-2; ferrocenylzinc chloride, 94161-76-9; diiodonaphthalene, 1730-04-7; ruthenocene, 1287-13-4; dilithioruthenocene, 60898-13-7; ruthenocenylzinc chloride, 113793-02-5; α-naphthylferrocene, 94161-77-0.

Synthesis, X-ray Structure, and Nucleophilic Properties of Mixed Bis(diene)tantalum Complexes Ta(η^5-C_5R_5)(η^4-C_4H_6)(η^4-C_6H_{10})

Takuji Okamoto, Hajime Yasuda,* and Akira Nakamura*

Department of Macromolecular Science, Faculty of Science, Osaka University, Toyonaka, Osaka 560, Japan

Y. Kai,* N. Kanehisa, and Nobutami Kasai*

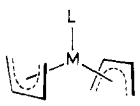
Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565, Japan

Received November 18, 1987

Mixed bis(diene) complexes of tantalum have been synthesized in a stepwise manner either by reaction of $TaCl_2L$(butadiene) of supine (exo) geometry (L = C_5Me_5, C_5H_5) with (2,3-dimethyl-2-butene-1,4-diyl)magnesium or by reaction of $TaCl_2L$(2,3-dimethylbutadiene) of supine geometry with (2-butene-1,4-diyl)magnesium. In the former reaction, the initial geometry of the coordinated diene changes from supine to prone (endo) while, in the latter reaction, the supine geometry of the 2,3-dimethylbutadiene ligand was maintained. Ta(C_5Me_5)(prone-butadiene)(supine-2,3-dimethylbutadiene) (**6a**) thus obtained crystallizes in space group *Pbca* with a = 14.173 (3) Å, b = 16.524 (3) Å, c = 15.344 (3) Å, and Z = 8. The reaction of **6a** with 2,4-dimethyl-3-pentanone revealed the higher reactivity of the butadiene unit lying prone compared with dimethylbutadiene lying supine.

Introduction

Bis(diene) complexes of group 5A early transition metals (Ta,[1] Nb[2]) of the type LM(diene)$_2$ (L = C_5H_5, C_5Me_5) were recently found to exhibit a novel supine–prone (exo–endo) structure (1),[3] where the metal–diene moieties consist of



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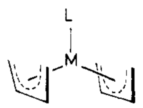

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