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Chiral Oxazolines Linked to Tetrathiafulvalene (TTF): Redox-Active Ligands for Asymmetric Synthesis

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Abstract: The syntheses of novel tetrathiafulvalene substituted chiral oxazolines **14** and **18** are reported. The application of these compounds as catalysts for asymmetric palladium-catalysed allylic substitution reactions has been investigated along with the solution electrochemical redox behaviour of **14a** in the presence of palladium ions. Copyright © 1996 Elsevier Science Ltd

INTRODUCTION

The control of enantioselectivity remains at the forefront of organic synthesis, and chiral ligands designed to control successfully the outcome of a reaction where two product enantiomers can be formed continue to be developed.[1] Of particular interest are those cases where a catalytic amount of a chiral modifier is employed in conjunction with an organometallic reagent and a prochiral substrate.[2] Our interest in developing systems in which an electrochemical response could be observed in a guest ligand when a metal was complexed[3] led us to postulate that a chiral ligand containing a redox active unit should be capable of performing a chiral transformation with the subsequent loss of the metallo - intermediate upon electrochemical oxidation, thus facilitating a catalytic cycle. We elected to employ oxazolines as the source of chirality, principally because since their inception[4] they have found widespread use in a variety of asymmetric reactions,[5] but also because they are readily accessible from homochiral amino alcohols. Recently, suitably substituted oxazolines have been employed as catalysts in Diels-Alder reactions,[6] asymmetric copper-catalysed cyclopropanations,[7] directed *ortho*-lithiation of ferrocenes[8] and hydrosilylation reactions of ketones with both rhodium[9a,b] and iridium[9c] catalysts. Of the recent developments utilising oxazolines however, those utilising a secondary donor atom (typified by ligands **1-5**) to modify palladium - catalysed allylic substitution reactions have proven most successful.[10] From our perspective, those incorporating a sulfur atom as an auxiliary donor ligand *i.e.* **1-4** were particularly attractive as we wished to employ tetrathiafulvalene (TTF) **6** as the redox active group, and it was envisaged that the dithiole sulfur atoms already contained within this unit could be utilised as secondary donors. By virtue of their redox properties, TTF and its derivatives have enjoyed widespread use as electron donor molecules for the formation of solid-state charge-transfer complexes and radical ion salts, many of which are molecular conductors,[11] and TTF has been used recently as a reagent in synthesis involving electron transfer reactions,[12] but it has not been used in the present context.
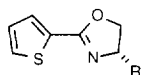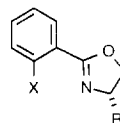

1 R = alkyl
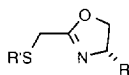
2 R = alkyl
R'= aryl, alkyl
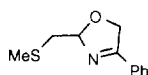
3

4 R = alkyl, X = ArS
**5** R = alkyl, X = Ph₂P

RESULTS AND DISCUSSION

The initially envisaged route was to apply the methodology described by Bölm[13] to convert nitriles into oxazolines. Thus, TTF **6** was converted to the known cyano derivative **7** *via* a lithiation protocol followed by treatment with tosyl cyanide.[14] All attempts to convert **7** to the oxazoline **9** with zinc dichloride

and 2-aminopropanol **8** were, however, unsuccessful, despite the use of prolonged reaction times and higher boiling solvents (Scheme 1). The lack of reactivity of the nitrile group of **7** is possibly due to the fact that it is conjugated to the dithiole ring and, therefore, possesses a resonance contribution from the sulfur lone pairs.

To circumvent this problem, β-hydroxy amides **13** were prepared in good yield from the corresponding commercially available homochiral amino alcohols **12** and tetrathiafulvalene carbonyl chloride **11**[15] (itself prepared from acid **10** which can be synthesised from TTF **6** on a multigram scale).[16] The hydroxy amides **13** were subsequently cyclised and dehydrated under Appel conditions[17] with PPh₃, CCl₄ and Et₃N affording the novel homochiral[18] tetrathiafulvalenyl oxazolines **14** in reasonable yields, as shown in Scheme 1.

| 12-14	a R = ⁱPr	49%	59%
	b R = Ph	73%	74%
	c R = ᵗBu	51%	68%
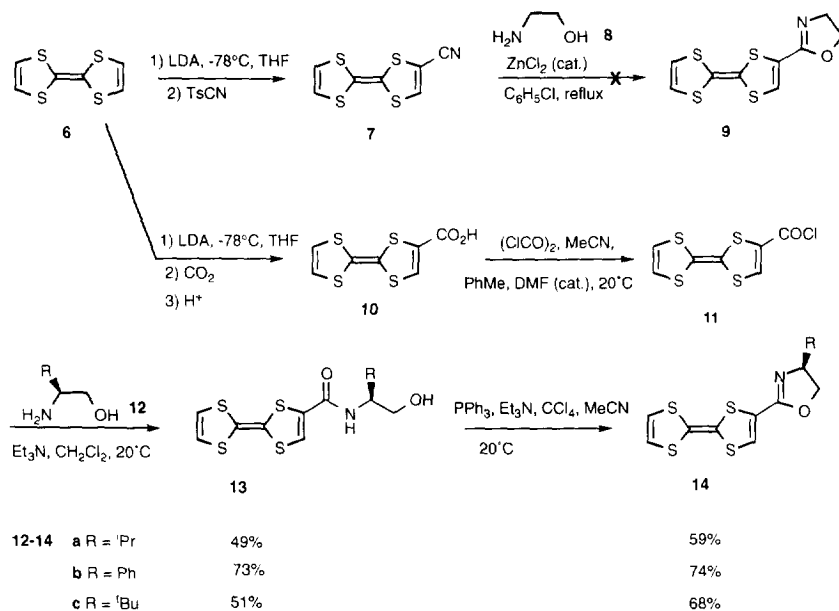
Scheme 1

In order to determine whether an oxazoline tethered to an auxiliary donor ligand by a rigid conjugated spacer unit would be effective as a ligand in our studies, system **18** was synthesised as outlined in Scheme 2. Thus, oxazoline **15**, prepared by a modification of the methodology developed by Meyers,[19] was converted into the unstable Wittig-Horner reagent **16** which could be isolated, but was preferably used immediately and reacted with aldehyde **17**[16] to afford the π-extended *trans*-tetrathiafulvalenyl oxazoline **18** in *ca* 50% yield (based on **17**.)
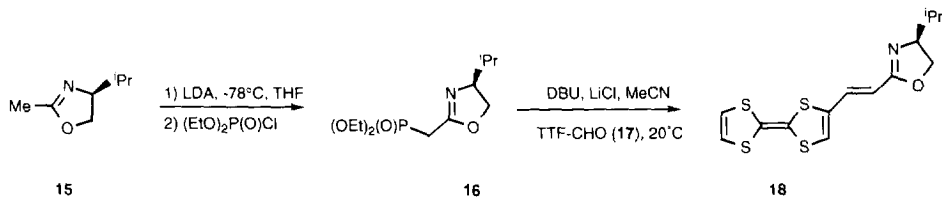
Scheme 2

With systems **14a-c** and **18** in hand, their application in palladium - catalysed allylic substitution reactions was investigated. Allylic actetate **19**[20] was reacted with the sodium salt of dimethyl malonate **20** in the presence of allylpalladium chloride (2.5 mol%) and the TTF-oxazoline derivative (10 mol%) in tetrahydrofuran to afford the substitution product **21** as shown in Scheme 3 and Table 1.

Scheme 3
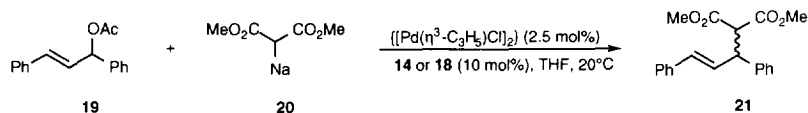
Table 1. Enantioselectivity in palladium-catalysed allylic substitution reactions using oxazolines **14** and **18**.

Run [a]	Ligand	Time (hr)	Yield (%) [b]	ee[c] of (-) **21** (%) [d]
1	**14a**	48	29	21
2	**14b**	48	28	17
3	**14c**	48	trace	------
4	**18**	72	trace	------

a) All reactions were 0.4 mM in acetate **19**. b) Yield of analytically pure product after column chromatography. c) Determined by ^{1}H-NMR spectroscopy in the presence of Pr(hfc)$_3$ for which a splitting of both methyl ester peaks was observed. d) Determined by optical rotation measurements compared to the value reported by Pfaltz *et al.*[21]

The low enantiomeric excess measured for these systems is in contrast to the results reported for ligands **1-4** which contain a sulfur atom as the auxiliary donor ligand.[10a,b] This is presumably due to the fact that in those systems, the sulfur atom is assumed to act as a π-acceptor and nucleophilic attack occurs *cis* to the better donor *i.e. trans* to the sulfur atom. This is in sharp contrast to the case of the 1,3-dithiole sulfur atoms of the TTF unit which are strong π-donors and the reaction will occur *cis* to them (*cf.* diastereomeric intermediates **22** and **23**). Notably, ligand **14b**, possessing a phenyl group in the 4-position does give some product in these reactions, whereas the corresponding thienyl ligand is reported to have no effect.[10b] Once again, this may be due to the fact that allylic substitution is occuring *cis* to the better π-donor (through intermediate **22**) and is thus not as sterically congested in the transition state as **23** (an intermediate analogous to that through which the thienyl ligands react). This effect will naturally lower the enantiomeric excess observed but will allow the reaction to proceed with bulkier substituents, the limitation being the *tert*-butyl group in ligand **14c**.
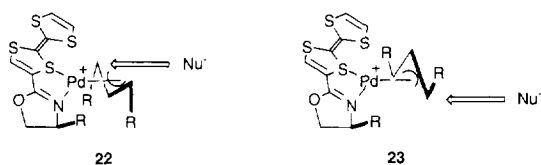
Crystallographic and NMR evidence has been published[22] which supports the hypothesis that with structurally similar catalysts the reaction proceeds through an intermediate analogous to **22** when the nitrogen atom is acting as the π-donor, and species **22** may, therefore, be an intermediate in our case.

The fact that the π-extended system **18** showed no ability to catalyse the reaction is not surprising given the rigidity of the alkene linkage and the increased distance between the oxazoline nitrogen and a sulfur atom in the dithiole ring. The low yields obtained from catalysts **14a,b** are most likely due to a strongly bound complex being formed *in situ* due to the strong electron-donating ability of the dithiole sulfur atoms. We explored whether altering the amount of palladium present and / or the palladium : ligand ratio would effect either the yield or the *ee* using **14a** as a standard chiral modifier. The results are summarised in Table 2.

Table 2. The change in enantioselectivity using oxazoline **14a** with various ratios with allypalladium chloride.

Entry	Ratio[a] Pd : **14a**	Time (h)	Yield (%) [b]	ee of (-) **21** (%) [c]
1	1 : 4	72	26	10
2	1 : 2.5	48	28	14
3	1 : 1	48	29	33
4	2 : 1	48	28	17
5[d]	1 : 1	24	41	33

a) Based on 2.5 mol% of palladium dimer (*i.e.* 5 mol% of palladium). b) Isolated homogeneous material after chromatography. c) Determined as in Table 1. d) Run using 5 mol% of palladium dimer (*i.e* 10 mol% palladium).

The optimum ratio of palladium : ligand appears to be 1:1 (entry 3) which affords the product with the highest enantioselectivity. Somewhat surprisingly, increasing the amount of ligand present (entries 1-2) actually results in a depreciation of the *ee*, which is in contrast to the observations of Williams *et al.*[10b] where an increase in Pd : ligand ratio resulted in an increase in the enantioselectivity. The use of an increased amount of palladium source (entry 5) did not effect the *ee* (*cf* entry 3) but did, as expected, increase the yield of the reaction since more of the active palladium intermediate is available.

The low affinity of previous ligands for palladium has been postulated as the reason why the enantioselectivities of many reactions fall in more polar solvents, due to the displacement of the ligand by a solvent molecule, whereas the yields in such reactions tend to rise.[10] The low yields observed with our systems may, however, be due to a more tightly bound complex, where turnover of the palladium is slow.

To investigate this possibility, titration studies using cyclic voltammetry measurements were performed to determine if any palladium binding could be detected in the redox behaviour of the systems. The titration of a standard solution of palladium acetate into a known concentration of **14a** in dry, degassed acetonitrile showed a significant cathodic shift in the electrochemical potential of the redox wave of the TTF system. The results are summarised in Table 3. Figure 1 demonstrates the difference in the cyclic voltammetric response of **14a** before and after the addition of twenty equivalents of palladium acetate to the solution.

The change in the half wave potential of the first redox wave $(E_1{}^{1/2})$ is most noticeable when ten equivalents of palladium were present: with each sequential addition the rate of change gradually decreased. This may be indicative of an initially formed species involving coordination of $Pd(OAc)_2$ to TTF being present in solution relatively early in the experiment. The change in the potential of the second wave $(E_2{}^{1/2})$ is significantly less than that of the first wave, presumably because the metal has been lost from the system as the TTF unit undergoes the first oxidation process, due to coulombic repulsion between the two adjacent positively charged sites, *i.e.* the palladium centre and the TTF radical cation.
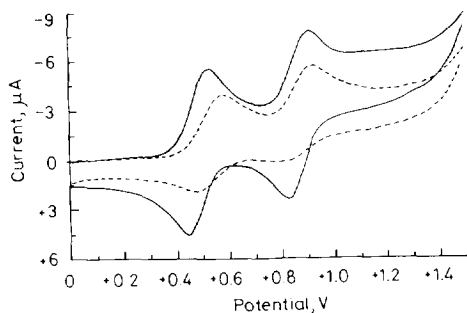

Figure 1.   Cyclic voltammogram of compound **14a** in acetonitrile before (–) and after (---) the addition of $Pd(OAc)_2$ (20 equivalents).

A qualitatively similar electrochemical response has been noted upon addition of metal salts to TTF derivatives bearing fused macrocycles.[3] It can be seen from Figure 1 that in addition to the change in oxidation potential of the first wave, the presence of palladium renders the TTF oxidations quasi-reversible, especially the second wave. (This is deduced from a reduction in the current passed on the anodic sweep). However, the fact that there is still a significant level of reversibility presents the opportunity for the metal to be released from the system electrochemically, thereby offering the possibility of a catalytic cycle being established.

Table 3. Electrochemical response of **14a** with added palladium acetate.

Equiv. of Pd(OAc)$_2$	$E_1^{1/2}$ / mV	$E_2^{1/2}$ / mV	$E_2^{1/2}$ - $E_1^{1/2}$ / mV
0	520	910	390
10	560	920	360
20	580	920	340
30	590	920	330

CONCLUSIONS

The synthesis of a number of homochiral oxazolines appended to TTF has been accomplished. The sulfur atoms of the TTF system have been observed to act as secondary ligands in palladium-catalysed allylic substitution reactions where they provide the π-donor required to accomplish an electronic bias in the reaction intermediate. These compounds do not provide the levels of enantioselectivity observed where a sulfur atom acts as a π-acceptor, presumably due to the increased distance between the reactive site and the chiral group on the oxazoline ring. Cyclic voltammetric studies indicate that there is a quasi-reversible interaction between a palladium source and oxazoline **14a**, suggesting that the binding of the palladium to this ligand may be controlled electrochemically. Further studies on these systems, including modification of the π-donor ability of the TTF and electrochemical recycling of the catalyst, are in progress and will be reported in due course.

EXPERIMENTAL

^{1}H NMR spectra were obtained on a Varian Gemini 200 spectrometer operating at 200.10 MHz. Mass spectra were recorded on a VG7070E spectrometer operating at 70eV. Infra-red spectra were recorded on a Perkin-Elmer 1615 FTIR operated from a Grams Analyst 1600. Optical rotation measurements were performed using an Optical Activity AA - 10 polarimeter. Melting points were obtained on a Kofler hot-stage microscope apparatus and are uncorrected. All reagents were of commercial quality and solvents were dried, where necessary, using standard procedures.

Cyclic voltammetric data were measured with iR compensation using a BAS CV50 electrochemical analyser. The experiments were carried with 5 mL of a *ca.* 10^{-4} M solution of compound in acetonitrile containing 0.2 M tetrabutylammonium hexafluorophosphate (Fluka, puriss, electrochemical grade) as the supporting electrolyte. The potentials were measured versus platinum wire quasi-reference electrode and corrected versus ferrocene/ferrocinium$^+$ as $E^{1/2}$ = +0.36V by adding ferrocene to the solution after the experiment and referenced versus Ag/AgCl. Satisfactory elemental analysis were obtained for all new compounds (CHN ± 0.3%).

General Procedure for β-hydroxy amides 13

To a well stirred solution of the amino alcohol **12** (1.6 mmol) and dry triethylamine (2.6 mmol) in anhydrous dichloromethane (5 ml) was added a solution of freshly prepared tetrathiafulvalene carbonyl chloride **11**[15] (350 mg, 1.3 mmol) in anhydrous dichloromethane (5 ml). The resultant solution was stirred under argon at 20°C overnight before being diluted with dichloromethane (50 ml) and washed with water (2 x 25 ml). The organic phase was separated, dried (MgSO$_4$) and the solvent removed *in vacuo* to afford a dark brown solid. Column chromatography using silica gel (70-230 mesh) and 5% methanol in dichloromethane as the eluting solvent afforded the desired products. There were thus obtained:

(2S)-N-(1-hydroxy-3-methylbutyl)tetrathiafulvalenamide **13a**, from (S)-valinol (160 mg) an orange solid (210 mg, 49%) mp. 99-101°C; δ_H (CDCl$_3$) 0.96 (3H, d, J = 5.2 Hz), 1.00 (3H, d, J = 5.2 Hz), 1.95 (1H, sextet, J = 5.2, 2.1 Hz), 2.50 (1H, bs), 3.75 (2H, d, J = 5.0 Hz), 3.80 (1H, m), 5.90 (1H, bd, J = 5.0 Hz), 6.33 (2H, s) and 7.13 (1H, s); ν_{max} (KBr)/cm^{-1} 3254, 2964, 1608, 1567, 1546 and 1029; m/z (DCI) 334 (MH$^+$, 100%); α_D (20°C, dichloromethane, c= 0.1, α = -47°); CV E$^{1/2}$ +520 and +930 mV (both reversible).

(2S)-N-(1-hydroxy-3-phenylethyl)tetrathiafulvalenamide **13b**, from (S)-2-phenylglycinol (210 mg) a yellow-orange solid (348 mg, 73%) mp. 79-81°C; δ_H (CDCl$_3$) 2.15 (1H, m), 3.95 (2H, t, J = 4.6 Hz), 5.1 (1H, bs), 6.25 (1H, bd, J = 6.5 Hz), 6.34 (2H, s), 7.15 (1H, s) and 7.35 (5H, m); ν_{max} (KBr)/cm^{-1} 3305, 3060 1624, 1546, and 1053; m/z (DCI) 368 (MH$^+$, 100%); α_D (20°C, dichloromethane, c= 0.05, α = +87°); CV E$^{1/2}$ +510 and +900 mV (both reversible).

(2S)-N-(1-hydroxy-3,3-dimethylbutyl)tetrathiafulvalenamide **13c**, from (S)-tert-leucinol (150 mg) obtained as an orange solid (230 mg, 51%) mp. 169-171°C; δ_H (CDCl$_3$) 1.00 (9H, s), 2.05 (1H, t, J = 4.5 Hz), 3.67 (1H, t, J = 4.5 Hz), 3.90 (2H, m), 5.70 (1H, bs), 6.34 (2H, s) and 7.15 (1H, s); ν_{max} (KBr)/cm^{-1} 3310, 2966, 2920, 1616, 1564, and 1104; m/z (DCI) 330 (MH$^+$, 65%) and 154 (100%); α_D (20°C, dichloromethane, c= 0.2, α = -53°); CV E$^{1/2}$ +480 and +890 mV (both reversible).

General Procedure for oxazolines 14

To a solution of the approriate β-hydroxy amide **13** (0.55 mmol) in anhydrous acetonitrile (15 ml) under argon, were added sequentially dry triethylamine (2.3 mmol, 0.32 ml), triphenylphosphine (1.9 mmol, 0.72 g) and dry carbon tetrachloride (5 mmol, 0.5 ml). The resultant mixture was stirred at room temperature for 12 h, diluted with dichloromethane (50 ml) and washed with water (2 x 50 ml). The organic phase was separated, dried (MgSO$_4$) and the solvent removed *in vacuo* to afford a dark oil, column chromatography of which using silica gel (70-230 mesh) and hexane/dichloromethane (3:1 v/v) as the eluting solvent afforded the desired products. There were thus obtained:

(S)-2-tetrathiafulvalenyl-4-(1-methylethyl)oxazoline **14a** from **13a** (180 mg) an orange solid (102 mg, 59%) mp. 124-126°C; δ_H (CDCl$_3$) 0.97 (3H, d, J = 4.6 Hz), 1.00 (3H, d, J = 4.6 Hz), 1.95 (1H, sextet, J = 4.6, 2.1 Hz), 3.70 (2H, t, J = 5.0 Hz), 4.00 (1H, m), 6.45 (2H, s) and 7.10 (1H, s); ν_{max} (KBr)/cm^{-1} 1628, 1508, 1308 and 1274; m/z (DCI) 316 (MH$^+$, 100%); α_D (20°C, dichloromethane, c= 0.1, α = -67°); CV E$^{1/2}$ +510 and +920 mV (both reversible).

(S)-2-tetrathiafulvalenyl-4-phenyl-oxazoline **14b** from **13b** (190 mg) an orange-yellow solid (123 mg, 68%) mp. 104-107°C; δ_H (CDCl$_3$) 4.21 (1H, t, J = 8.3 Hz), 4.75 (1H, t, J = 8.3 Hz), 5.33 (1H, t, J = 8.3 Hz), 6.33 (2H, s), 7.10 (1H, s) and 7.3 (5H, m); ν_{max} (KBr)/cm^{-1} 1627, 1534, 1357 and 1007; m/z (DCI) 350 (MH$^+$, 100%); α_D (20°C, dichloromethane, c= 0.2, α = +106°); CV E$^{1/2}$ +500 and + 890 mV (both reversible).

(S)-2-tetrathiafulvalenyl-4-(2,2-dimethylethyl)oxazoline **14c** from **13c** (200 mg) a yellow solid (142 mg, 74%) mp. 96-98°C; δ_H (CDCl$_3$) 0.90 (9H, s), 3.95 (1H, t, J = 4.5 Hz), 4.20 (2H, m), 6.30 (2H, s) and 6.95 (1H, s); ν_{max} (KBr)/ cm^{-1} 1641, 1540, 1358 and 1017; m/z (DCI) 348 (MH$^+$, 20%) and 117 (100%); α_D (20°C, dichloromethane, c= 0.2, α = -76°); CV E$^{1/2}$ +480 and +890 mV (both reversible).

(4S)-4-(1-methylethyl)-2-methyl-2-oxazoline **15**. To a stirred solution of ethyl acetimidate hydrochloride (2.6 g, 20 mmol) in dichloromethane (10 ml) at 0°C was added (S)-valinol (1.75 g, 17 mmol) in dichloromethane (10 ml). The resultant mixture was allowed to warm to room temperature, stirred overnight, poured into water (50 ml) and extracted with dichloromethane (3 x 50 ml). The combined organic phases were separated, dried (MgSO$_4$) and the solvent removed by distillation at atmospheric pressure. Distillation of the residue gave **15** (1.72g, 80%) as a colourless oil, bp. 110-115°C; δ_H (CDCl$_3$) 0.87 (3H, d, J = 5.4 Hz), 0.97 (3H, d, J = 5.4 Hz), 1.70 (1H, m), 1.97 (3H, d, J = 1 Hz), 3.90 (2H, m) and 4.2 (1H, t, J = 6.4 Hz); ν_{max} (film)/cm^{-1} 3000, 1675, 1320 and 1234; m/z (DCI) 128 (MH$^+$, 100%).

(4S)-4-(1-methylethyl)-2-[(E)-1-tetrathiafulvalenyl]-2-oxazoline **18**. To a well-stirred solution of lithium diisopropylamide (8.3 ml of a 1.5M solution in THF) in dry THF (20 ml) at -78°C under argon, was added a solution of oxazoline **15** (318 mg, 2.5 mmol) in tetrahydrofuran (10 ml). The mixture was stirred for 1h whereupon diethyl chlorophosphate (0.43 ml, 3 mmol, 1.2 equiv.) was added. After stirring for an additional 1h, the mixture was warmed to 0°C and quenched by the addition of saturated ammonium chloride solution

(20 ml). The mixture was poured into water (100 ml), extracted with diethyl ether (3 x 50 ml), dried (MgSO$_4$) and the solvent removed *in vacuo* to afford the crude phosphonate **16** (0.6 g) as a yellow oil. To a solution of **16** (0.6 g, 2.3 mmol), lithium chloride (75 mg, 1.8 mmol) and DBU (0.23 ml, 4.3 mmol) in dry acetonitrile (50 ml) was added TTF-carbaldehyde **17** (0.38 g, 1.6 mmol). The mixture was stirred under argon overnight at 20°C, poured into water (100 ml) and extracted with dichloromethane (3 x 50 ml). The organic phases were combined, dried (MgSO$_4$) and the solvent removed *in vacuo* to afford a brown solid, column chromatography of which on silica gel (70-230 mesh) eluting with hexane/dichloromethane (1:1 v/v) afforded **18** as an orange solid (0.24 g, 48%) mp. 110-112°C; δ_H (CDCl$_3$) 0.90 (3H, d, J = 3.5 Hz), 1.00 (3H, d, J = 3.5 Hz), 1.95 (1H, sextet, J = 3.5, 1.6 Hz), 4.00 (2H, t, J = 4.1 Hz), 4.29 (1H, m), 5.95 (1H, d, J = 15.8 Hz), 6.32 (2H, s), 6.54 (1H, s) and 7.00 (1H, d, J = 15.8 Hz); ν_{max} (KBr)/cm^{-1} 2953, 1640, 1596, 1522, 1458, 1355, 1251 and 988; m/z (DCI) 342 (MH$^+$, 100%); α_D (20°C, dichloromethane, c= 0.1, α = -56°); CV E$^{1/2}$ +535 and + 970 mV (both reversible).

Typical Procedure for Palladium-Catalysed Allylic Substitution. To {[Pd(η_3-C$_3$H$_5$)Cl]$_2$} (4 mg, 0.01 mmol) was added a solution of the ligand **14** or **18** (0.04 mmol) in anhydrous THF (1 ml) and racemic-(E)-1,3-diphenylprop-2-enyl acetate **19**[18] (106 mg, 0.4 mmol). The solution was stirred at room temperature under argon for 15 min whereupon dimethyl sodiomalonate **20** (64 mg, 0.4 mmol) in anhydrous tetrahydrofuran (2 ml) was added. The reaction mixture was stirred for the time noted in Tables 1 and 2, whereupon it was diluted with diethyl ether (50 ml) and washed with saturated ammonium chloride (2 x 25 ml). The organic phase was separated, dried (MgSO$_4$) and the solvent removed *in vacuo* to afford a colourless oil. Column chromatography on silica gel (70-230 mesh) with hexane/diethyl ether (3:1 v/v) afforded **21** which was identical to that described in the literature[19].

Cyclic Voltammetric Titration Studies. A standard solution of **14a** was prepared (10^{-4}M in dry acetonitrile containing 10^{-2}M tetrabutylammonium hexafluorophosphate). A degassed 5 ml sample of this solution was employed in the subsequent studies. To this standard sample were added sequentially aliquots (0.5 ml, 10 equiv.) of a 10^{-2}M solution of palladium acetate in dry acetonitrile containing 10^{-2}M tetrabutylammonium hexafluorophosphate. The cyclic voltammogram was recorded in each case with internal resistance (iR) compensation and corrected versus ferrocene/ferrocene$^+$ as E$^{1/2}$ = +0.36V. Additions proceeded until no further change in the voltammogram could be observed.

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