Synthesis of 2,6-Bis(2-oxazolinyl)phenylplatinum(II) NCN Pincer Complexes by Direct Cyclometalation. Catalysts for Carbon−Carbon Bond Formation

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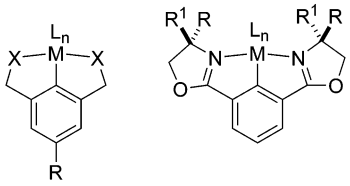
1,3-Bis(4′,4′-dimethyl-2′-oxazolinyl)benzene (**5a**) and 5-nitro-1,3-bis(4′,4′-dimethyl-2′-oxazolinyl)benzene (**5b**) were heated in dry acetic acid with K_2PtCl_4 to give the corresponding 2,6-bis(4′,4′-dimethyl-2′-oxazolinyl)phenylplatinum(II) chloride complexes **6a** and **6b** in 49 and 11% yield, respectively. The X-ray structure of **6b** is reported. The main side product observed in the platination of **5a** was identified as di(2-methyl-2-*N*-acetyl)propyl isophthalate. In contrast, use of $Pd(OAc)_2$ with **5a** in this protocol, followed by addition of LiBr, gave 2,6-bis(4′,4′-dimethyl-2′-oxazolinyl)phenylpalladium(II) bromide in only 3% yield. Treatment of **6a** with AgOTf and $AgSbF_6$ in acetone gave quantitatively the corresponding cationic 2,6-bis(4′,4′-dimethyl-2′-oxazolinyl)phenyl(aquo)platinum(II) complexes **15a** and **15b**. Similarly treatment of **6b** with AgOTf in acetone gave 4-nitro-2,6-bis(4′,4′-dimethyl-2′-oxazolinyl)-phenyl(aquo)platinum(II) trifluoromethanesulfonate (**15c**) (72%). Complexes **15a**−**c**, together with 2,6-bis(4′,4′-dimethyl-2′-oxazolinyl)phenylaquopalladium(II) triflate (**15d**), were applied as catalysts for the Michael reaction between methyl vinyl ketone and ethyl cyanoacetate and the Diels−Alder reaction between acrylonitrile and cyclopentadiene. In both cases platinum complex **15a** was found to be the most active, with the 4-nitro group of **15c** resulting in decreased catalytic activity.

Introduction

Organometallic pincer complexes of general structure **1** are air-stable and versatile compounds that are attracting widespread interest in catalysis and materials science.[1] A major subcategory are 1,3-bis(2′-oxazolinyl)phenyl systems **2** containing a variety of late transition metals.[2] Their ready availability from homochiral amino alcohols, and resulting C_2-symmetry, has been exploited with these systems acting as both catalysts[2a,c,e−g,i,j] and stoichiometric controllers[2d] for a number of asymmetric organic transformations.



1 **2** M = Pd^{II}, Pt^{II}, Pt^{IV}, Rh^{III}

Complexes **2** are obtained either by oxidative addition to a precursor 2-halo[2a] or 2-stannyl-1,3-bisoxazoline[2j] or by transmetalation with a 2-lithio[2c,f] or 2-stannyl[2b,d] organometallic. We recently reported, in contrast to these requirements for 1,2,3-trisubstituted building blocks, a simpler method using direct cyclometalation of 1,3-bis(imino)benzenes (Scheme 1).[3] Similarly, 1,3-bis(2-pyridinyl)benzene has also been found to undergo selective 2-platination under the same conditions.[4] In contrast, palladation of these same substrates gave predominantly 4-palladated or 4,6-dipalladated products.[5] In this paper we report on the use of 1,3-bis(2′-oxazolinyl)benzenes in this direct metalation protocol and on the application of the resulting platinum pincer complexes as catalysts for C−C bond formation.

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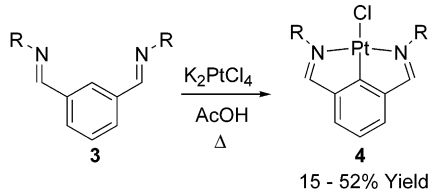
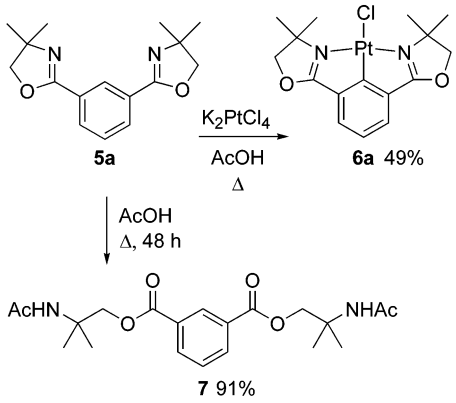
Scheme 1



Scheme 2



Results and Discussion

A mixture of bisoxazoline **5a**,[6] potassium tetrachloroplatinate, and acetic acid were heated at reflux for 48 h (Scheme 2). Solvent removal and column chromatography resulted in isolation of a yellow crystalline solid identified as pincer complex **6a** by (i) the absence of the one proton singlet in the ^{1}H NMR spectrum, (ii) the reduction in ν(C=N) by 42 cm^{-1} compared to **5a** (1651 vs 1609 cm^{-1}) indicative of both nitrogens coordinating to the new metal center, and (iii) ^{195}Pt coupling in both the ^{1}H and ^{13}C NMR spectra consistent with that previously observed in **4**.[3] The yield of **6a** was found to be highly dependent on the dryness of the acetic acid employed. Commercial acetic acid of 99.8% purity gave a maximum yield of no more than 21%. Following distillation of this acetic acid from P_2O_5 (approximately 1 wt %/vol) and acetic anhydride (approximately 1% vol/vol), under a nitrogen atmosphere, the yield of **6a** increased to a replicable 49%. Heating **5a** in acetic acid without the platinum salt gave predominantly a single compound identified as the oxazoline ring-opened diester **7**. This was also observed, together with **6a**, on examination of the crude platination reaction mixture by ^{1}H NMR. It is of note that this did not contain any other platinated products of significant quantity; thus the yield of **6a** appears to be limited only by competitive reaction of the oxazoline rings with acetic acid. Accordingly, a range of other solvents were investigated by heating **5a** and K_2PtCl_4 at reflux under nitrogen for 48 h in ^{i}PrOH, dioxane, CH_3CN, C_6H_5Cl, toluene, or DMSO. Examination of the ^{1}H NMR spectra of the resulting crude reaction mixtures revealed no evidence for the formation of **6a**. Reaction in DMF resulted in a detectable amount of **6a** in the crude ^{1}H NMR spectrum (<2%), which could not be isolated by column chromatography. Heating at reflux open to the atmosphere in water for 48 h gave **6a** in 17% isolated yield; repetition under an inert atmosphere gave no improvement in yield. Examination of the crude reaction mixture in this instance revealed, in addition to **6a**, a small quantity of unreacted starting material **5a** and a multitude of other organic products. Various mixtures of AcOH/H_2O gave only **7**.

In catalysis, group 10 metal containing NCN pincer complexes have primarily been used as Lewis acids with nitrile (Michael,[2c,f,3,7] Diels−Alder[3])- and isonitrile (aldol[2i,8])-containing substrates. We anticipated that introduction of an electron-withdrawing nitro group *para* to platinum would increase the Lewis acidity of the resulting catalyst. Related platinum and palladium NCN pincer complexes containing a *para*-nitro substituent (NCN = 2,6-(Me_2NCH_2)-4-$NO_2C_6H_2$) have recently been reported by van Koten and co-workers, obtained by oxidative addition of Pt(0) and Pd(0), respectively, into the corresponding aryl bromide.[9] Thus oxazoline **5b**, readily available from commercially available 5-nitroisophthalic acid **8** (Scheme 3), was platinated using the procedure described above to give the pincer complex **6b** in 11% isolated yield (use of acetic acid of 99.8% purity without specific drying gave a maximum 4% yield). The structure of this new complex was confirmed by an X-ray crystal structure analysis (Figure 1). A related structure of general formula **2** (M = Pt, L_n = Cl, R = ^{i}Pr, R^1 = H)[2d] lacking any *para* functionality shows essentially the same bond lengths and angles for the metal coordination sphere except for a longer Pt−Cl bond (2.379(3) Å). The shorter Pt−Cl bond length in **6b** compared to **2** reveals that a *para*-nitro group results in a reduced *trans* influence. Comparison to the corresponding palladium complex **2** (M = Pd, L_n = Cl, R = ^{i}Pr, R^1 = H)[2i] reveals a significantly longer Pd−Cl bond length (2.391(3) Å), consistent with the smaller ionic radius of Pt(II) versus Pd(II). The X-ray analysis of **1** (M = Pt, X = $N(Me)_2$, R = NO_2, L_n = Br)[9b] shows no difference in Pt−C bond length; the Pt−N bonds (2.105(3) and 2.099(2) Å) are longer than **6b**, and the N−Pt−N angle (163.20(11)°) is also larger than in **6b**, the differences being due to the conjugated, coplanar nature of the NCN ligand in **6b**.

It has previously been reported that palladation of (*R*,*R*)-1,3-bis(2′-(4′-ethyl)oxazolinyl)benzene (**11**) with palladium acetate in either acetic acid or $CHCl_3$, followed by the addition of lithium bromide, resulted in the formation of pincer complex **12** in 45% yield.[10] As this method appeared complementary to the platination protocol described above, we attempted the corresponding palladation of **5a**. Heating this at reflux with Pd(OAc)$_2$ in acetic acid under a nitrogen atmosphere, followed by the addition of LiBr, gave impure complex **6c** in only 3% yield following isolation by column chromatography (Scheme 4). Repetition of the pallada-

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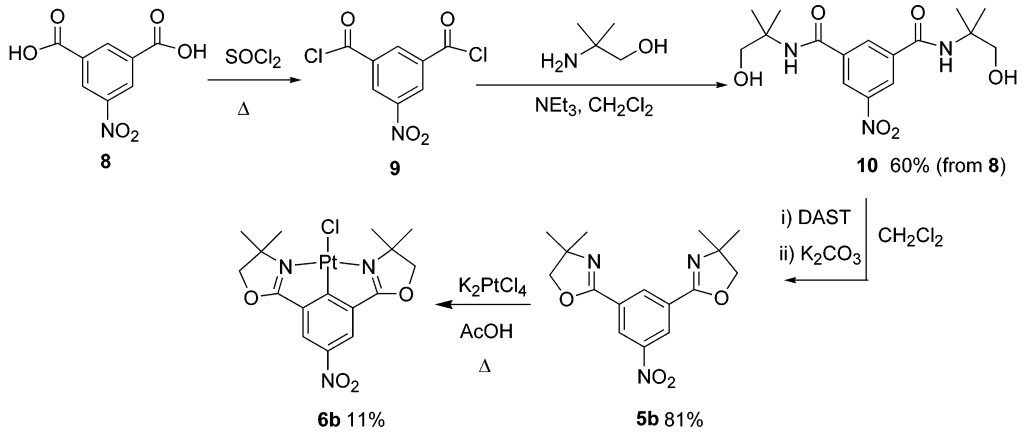
Scheme 3



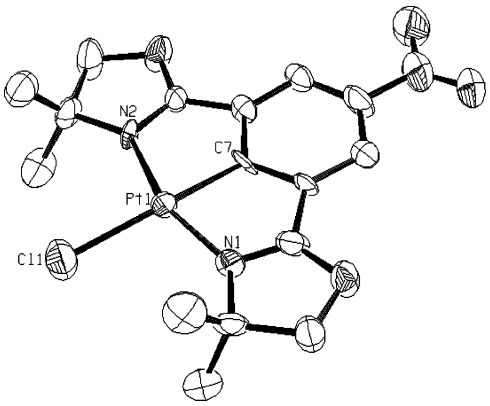
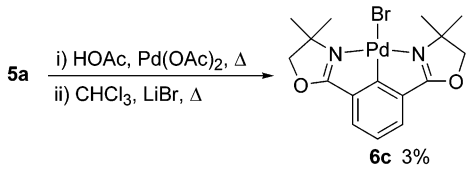
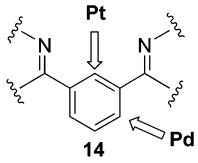


Figure 1. Representation of one of the two independent crystal structures of **6b**. Selected bond distances (Å) and angles (deg) are as follows (corresponding values for the unshown second structure are given in brackets): Pt(1)−Cl(1) = 2.350(5) [2.355(5)], Pt(1)−C(7) = 1.892(14) [1.909-(15)], Pt(1)−N(1) = 2.026(10) [2.035(11)], Pt(1)−N(2) = 2.034(9) [2.038(9)], C(7)−Pt(1)−N(1) = 80.6(5) [79.5(6)], C(7)−Pt(1)−N(2) = 80.3(5) [79.2(6)], C(7)−Pt(1)−Cl(1) = 179.4(5) [178.9(4)], N(1)−Pt(1)−N(2) = 160.9(5) [158.7(5)].

Scheme 4



tion in $CHCl_3$ did not yield any of the pincer complex **6c**, previously synthesized in our own group by a lithiation, palladium transmetalation procedure.[2f] Subsequent examination of the reported ^{1}H NMR data of the product formed on palladation of **11**[10] revealed inconsistencies with the range of C_2-symmetric complexes of general formula **2** (M = Pd^{II}, L_n = Br) that we have also previously synthesized.[2f] In particular *four* methyl triplets (J 6.5−7.7) are reported for the ^{1}H NMR spectrum, in contrast to the single triplet expected for a C_2-symmetric complex. We have never noted any deviation from this C_2 arrangement on examination of these complexes in solution by ^{1}H/^{13}C NMR. Furthermore, for a range of these complexes 4-H is observed in the ^{1}H NMR spectra between 7.08 and 7.17 ppm (t, J 7) and 3- and 5-H between 7.22 and 7.30 ppm (d, J 7).[2f] For the product arising from the palladation of **11** the ^{1}H NMR data for the aromatic region, also recorded in $CDCl_3$, is reported as 7.53 ppm (m) and 8.01 ppm (pdd).[10] Thus these workers cannot have isolated **12** as the major palladation product. The reported data are however consistent with the 4-palladated product **13**, present as a mixture of *cis* and *trans* isomers previously observed in related halogen-bridged palladacycles.[11] This outcome is in agreement with a trend for platination of 1,3-disubstituted benzenes of structure **14** proceeding at position 2; palladation in contrast leads to predominantly 4-substitution and/or 4,6-disubstitution.[3,4]

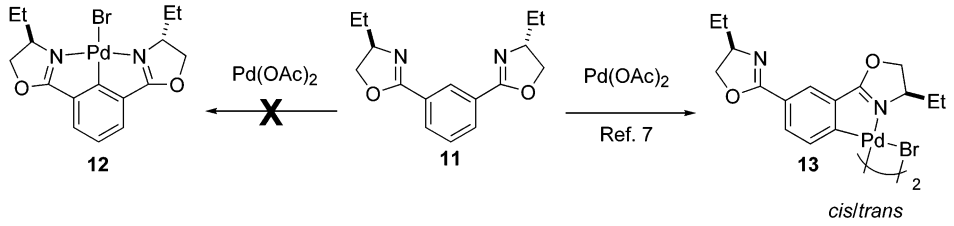


Halide abstraction on **6a**−**c** proceeded cleanly in acetone with $AgSbF_6$ and/or AgOTf to give platinum cationic complexes **15a**−**c** and palladium complex **15d**[2f] (Scheme 6). The presence of metal-coordinated water in these complexes was revealed by ^{1}H NMR spectroscopy, an observation in agreement with previously determined X-ray structure analyses of related cationic platinum and palladium complexes.[2d,f,i] Complex **15b** was found to be particularly hydroscopic and discolored within a few days.

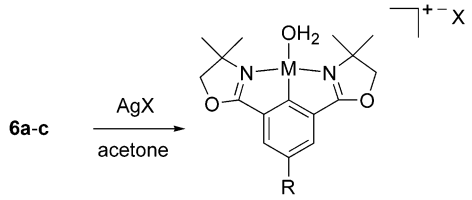
The availability of these platinum complexes permitted an analysis of their potential as Lewis acid catalysts for the transformation of nitrile-containing substrates. We have previously reported that palladium complexes similar to **15d** catalyze the Michael reaction between α-nitrile esters and unsaturated carbonyls[2c,f] and that platinum bisimine complex **16** also catalyzes this reaction and the Diels−Alder reaction between cyclopentadiene and acrylonitrile.[3] We wished to determine if there was any significant difference in the effectiveness of the two nitrogen-containing functionalities (imine vs oxazoline) with respect to catalysis of these reactions, and in particular to compare the relative effectiveness of platinum versus palladium. In addition, and as already

(11) For example, di-μ-chloro[(η^5-(*S*)-($_p$*R*)-2-(isopropyl)oxazolinyl)-cyclopentadienyl, 1-*C*,3′-*N*))-(η^4-tetraphenylcyclobutadiene)cobalt]dipalladium exists as a 1:0.7 mixture of isomers in $CDCl_3$, as determined by ^{1}H NMR: Overman, L. E.; Owen, C. E.; Pavan, M. M.; Richards, C. J. *Org. Lett.* **2003**, *5*, 1809.

Scheme 5



Scheme 6



15a M=Pt, X=OTf, R=H >99%
15b M=Pt, X=SbF_6, R=H 99%
15c M=Pt, X=OTf, R=NO_2 72%
15d M=Pd, X=OTf, R=H 52%

Scheme 7

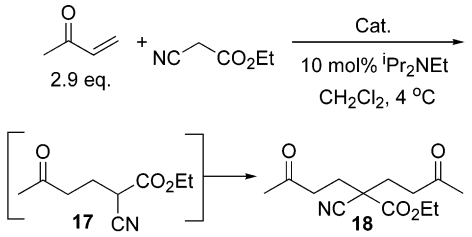


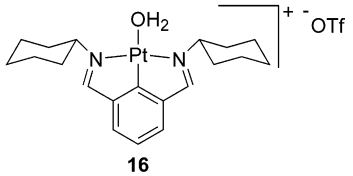
Table 1. Rates of the Michael Reaction between Ethyl Cyanoacetate and Methyl Vinyl Ketone

catalyst (mol %)	k_{obsd} [$\times 10^{-4}$ s^{-1}][a]	$t_{1/2}$ (h)[b]
15a (5%)	2.5	0.8
15b (5%)	2.7	0.7
15c (5%)	0.3	6.4
15d (5%)	0.58	3.3
16 (5%)	0.58	3.3
15a (1%)	0.012	16.5
none	0.083	23.1

[a] Determined by plotting $-\ln([CN]/[CN]_0)$ versus time (s) where CN = ethyl α-cyanoacetate. [CN] determined by ^{1}H NMR spectroscopy; see Supporting Information. [b] $t_{1/2} = \ln 2/(k \times 3600)$.

mentioned, we wished to determine if the presence of the 4-nitro substituent of **15c** significantly influenced catalyst effectiveness.

First, the Michael reaction between ethyl cyanoacetate and methyl vinyl ketone was studied as a function of cationic pincer complexes **15a**−**d** and **16** (Scheme 7, Table 1).



16

Under the common conditions used of 5 mol % catalyst and 10 mol % Hünig's base, the highest rates were observed with platinum oxazolines **15a**/**b**, revealing no significant differences between triflate and hexafluoroantimonate counterions. Palladium oxazoline **15d** and platinum imine **16** gave identical and slightly lower rates of conversion relative to the platinum oxazolines. Significantly, platinum oxazoline complex **15c** containing the *para*-NO_2 group proved to be the least effective catalyst. For **15a** at 1 mol % there is only a small enhancement over the background reaction. In each reaction the mono Michael adduct **17**[3] was observed in small quantities during the early stages of the reaction (see Supporting Information for more details).

Scheme 8

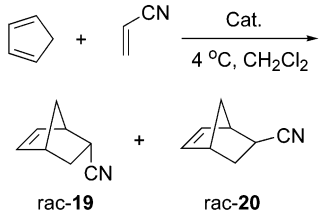


Table 2. Rates of the Diels−Alder Reaction between Cyclopentadiene and Acrolylnitrile

catalyst (mol %)	k_{obsd} [$\times 10^{-5}$ s^{-1}][a]	$t_{1/2}$ (h)[b]
15a (6%)	2	10
15b (6%)	0.7	28
15c (6%)	0.5	39
15d (6%)	0.5	39
16 (6%)	0.5	39
none	0.1	193

[a] Pseudo first order rate constant determined by plotting $-\ln([CN]/[CN]_0)$ versus time (s) where CN = acrolylnitrile. [CN] determined by ^{1}H NMR spectroscopy; see Supporting Information. [b] $t_{1/2} = \ln 2/(k \times 3600)$.

We next applied this same series of complexes to the Diels−Alder reaction between cyclopentadiene and acrylonitrile (Scheme 8).

Table 2 reveals the similar and relatively modest increases in the rate of formation of **19** and **20** promoted by complexes **15a**−**d** and **16**. Again platinum oxazoline **15a** gave the highest rate of reaction; in this instance the corresponding hexafluoroantimonate salt **15b** was slightly less effective. Complexes **15c**/**d** and **16** were essentially identical in their activity. In the absence of a catalyst, the *endo*:*exo* ratio of **19** and **20** is 1.5:1, which increases to 2.1:1 with **15a**/**b** and **16** and to 2.2:1 with **15c**/**d**. Catalysis of these two reactions (Schemes 7 and 8) was further attempted with **6b**. No acceleration over the background reaction was observed, revealing the requirement for halide abstraction.

The magnitude of Lewis acid activation of a carbonyl substrate has been determined by measurement of the downfield chemical shift that occurs in the ^{1}H NMR spectrum of crotonaldehyde when combined with the

Table 3. Determination of Relative Lewis Acidity of Complexes 15a−d

complex	^{1}H NMR of $NCCH_3$
none	1.93
15a	2.66[a]
15c	2.71[b]
15d	2.42
16	2.64[b]

[a] Doublet, $^4J_{PtH}$ 7.7 Hz. [b] Broad singlet.

Lewis acid under investigation.[12] To investigate the relative Lewis acidity of complexes **15a**,**c**,**d** and **16** a similar approach was taken whereby each was dissolved in CD_2Cl_2 (approximately 0.012 mmol/mL) and the ^{1}H NMR spectra were recorded after addition of 0.95 equiv of acetonitrile (Table 3). By this measure the platinum oxazoline complex **15a** is more acidic than its palladium congener **15d** and the platinum bisimine complex **16**. As expected, the *para*-nitro-substituted complex **15c** is the most Lewis acidic.

The available evidence supports the intermediacy of a metal-coordinated nitrile in the Michael reaction of ethyl cyanoacetate.[2f] Thus the higher activity of platinum oxazoline **15a** in this reaction, compared to palladium oxazoline **15d**, correlates with the higher Lewis acidity of the former with respect to nitrile substrates. This trend is also apparent in the Diels−Alder reaction of acrylonitrile. However, the correlation between Lewis acidity and reactivity does not extend to the *para*-nitro complex **15c**, the electron-withdrawing substituent having either no effect (Diels−Alder) or a detrimental effect (Michael) on the rate of these reactions.[13] Thus the activity of Lewis acidic NCN pincer catalysts is increased by using platinum rather than palladium and maybe decreased by introduction of an electron-withdrawing *para*-substituent. Bisoxazoline complexes are superior to bisimine complexes. Furthermore, as the substitution rate of platinum(II) complexes is several orders of magnitude slower than corresponding palladium(II) complexes,[14] nitrile exchange is clearly not rate determining in both of these reactions.

Conclusion

Reaction of 1,3-bis(2′-oxazolinyl)benzenes with K_2PtCl_4 in dry acetic acid provided direct access to bisoxazoline NCN pincer complexes. This protocol is a further example of the trend for cycloplatination of 1,3-disubstituted benzenes occurring at position 2 yielding NCN pincer complexes. In contrast, cyclopalladation of the same substrates fails to yield significant quantities of the corresponding pincer complex. The usefulness of this facile synthesis is reinforced by the higher activity displayed by platinum cationic complexes compared to their palladium counterparts when employed as Lewis acid catalysts for the Michael and Diels−Alder reaction of nitrile substrates. Introduction of a nitro substituent *para* to platinum resulted in higher Lewis acidity but reduced catalytic activity. We are currently investigating the application of these platinum Lewis acids as catalysts for the transformation of nitriles in other C−C bond forming reactions and extending the scope of this direct platination method to synthesize C_2-symmetric catalysts to engender stereocontrol in the Michael and Diels−Alder reactions.

Experimental Section

All organometallic reactions were performed under an atmosphere of nitrogen employing standard Schlenk techniques. Glacial acetic acid of 99.8% purity was dried by distilling from P_2O_5 and acetic anhydride. Dichloromethane was distilled from calcium hydride under nitrogen. Chloroform was distilled from calcium hydride under nitrogen. Other solvents employed were not specifically dried. Column chromatography was performed on SiO_2 (40−63 μm). Coupling to ^{195}Pt ($^xJ_{Pt}$) in the NMR data is reported as the 34% component of the signal. The Micheal and Diels−Alder reactions were carried out as previously described.[3]

Synthesis of 5-Nitro-1,3-bis[*N*,*N*′-(1′,1′-dimethyl-2′-hydroxylethyl)]benzenediamide, 10. Commercially available **8** (6.39 g, 0.03 mol) was refluxed in thionyl chloride (75 mL) for 48 h. Excess thionyl chloride was recovered by distillation in vacuo at 60 °C for 4 h, and cooling to room temperature afforded the previously reported **9**[15] as a colorless solid (>99% yield), which was used without further purification: IR (ν_{max}; CH_2Cl_2) 1756 (CO), 1535 (NO_2) cm^{-1}; ^{1}H NMR (δ; 270 MHz, $CDCl_3$) 9.09 (1H, t, *J* 1.6, Ar, 2-H), 9.19 (2H, d, *J* 1.6, Ar, 4- and 6-H). Diacid chloride **9** (7.42 g, 0.03 mol) was stirred at −78 °C in distilled dichloromethane (200 mL). 2-Amino-2-methyl-1-propanol (12.1 mL, 0.13 mol) was added over 15 min and stirring maintained for 30 min. Triethylamine (25 mL, 0.18 mol) was then added over 15 min, and the reaction mixture was stirred and allowed to slowly come to room temperature overnight. Solvent was removed in vacuo, the residue was taken up in ethyl acetate (100 mL) and washed with 2 M hydrochloric $acid_{(aq)}$ (3 × 100 mL), and the combined aqueous layers were extracted once more with ethyl acetate (100 mL). The ethyl acetate fractions were combined and washed with brine (1 × 250 mL), dried ($MgSO_4$), filtered, and dried in vacuo, then at 105 °C overnight, to give **10** (6.45 g, 60% yield). Mp: 174 °C. IR (ν_{max}; thin film) 3108 (NH), 3093 (OH), 1651 (C═O), 1566 (NO_2) cm^{-1}; ^{1}H NMR (δ; 270 MHz, d_6-acetone) 1.42 (12H, s, C*H*$_3$), 3.70 (4H, s, C*H*$_2$OH), 7.62−7.70 (2H, br s, O*H*), 8.57 (1H, t, *J* 1.5, Ar, 2-C), 8.58 (2H, d, *J* 1.5, Ar, 4- & 6-H), 8.72 (2H, s, N*H*); ^{13}C{^{1}H} NMR (δ; 68 MHz, d_6-DMSO) 23.1 (*C*H$_3$), 54.7 (*C*(CH$_3$)$_2$), 67.3 (*C*H$_2$), 124.6 (Ar, 4- and 6-C), 136.2 (Ar, 2-C), 141.1 (Ar, 1- and 3-C), 147.6 (Ar, 5-C), 168.5 (*C*═O); MS (*m*/*z*; FAB) 354 (MH$^+$, 12%); high-resolution MS (*m*/*z*, FAB), found for M + H 354.1650; $C_{16}H_{24}N_3O_6$ requires 354.1665.

Synthesis of 5-Nitro-1,3-bis(4′,4′-dimethyl-2′-oxazolinyl)benzene, 5b. To a stirred solution of **10** (4.5 g, 0.013 mol) in distilled dichloromethane (200 mL) at −78 °C under nitrogen was added diethylaminosulfur trifluoride (4.1 mL, 0.031 mol). Stirring was continued for a further 2 h, while the reaction mixture slowly warmed to room temperature. The reaction mixture was again cooled to −78 °C, and potassium carbonate (10.5 g, 0.076 mol) was added and the reaction stirred for a further 2 h while being allowed to warm to room temperature. The reaction mixture was washed with saturated sodium hydrogen carbonate solution (200 mL), which was added extremely cautiously, then with water (2 × 200 mL).

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(13) During the preparation of the manuscript, a report appeared on the application of R-substituted cationic complexes **1** (M = Pd, X = $N(Me)_2$, R = NO_2, L_n = OH_2, R = H, NO_2, NMe_2, COMe, OCH_2Ph, Ph, $SiMe_3$) to the Michael reaction between ethyl α-cyanoacetate and methyl vinyl ketone. This also reported the activity of the complex with R = NO_2 to be less than than that with R = H, which was the most active of the series: Dijkstra, H. P.; Slagt, M. Q.; McDonald, A.; Kruithof, C. A.; Kreiter, R.; Mills, A. M.; Lutz, M.; Spek, A. L.; Klopper, W.; van Klink, G. P. M.; Van Koten, G. *Eur. J. Inorg. Chem.* **2003**, 830.

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The organic fraction was separated, dried ($MgSO_4$), and filtered, and the solvent removed in vacuo to give **5b** as an off-white solid (3.46 g, 81% yield). Mp: 137 °C. Anal. Found: C, 57.00; H, 6.04; N, 12.37. Calcd for $C_{16}H_{19}N_3O_4 \cdot H_2O$: C, 57.30; H, 6.31; N, 12.53. IR (ν_{max}; CH_2Cl_2) 1659 (C═N), 1541 (NO_2) cm^{-1}; ^1H NMR (δ; 270 MHz, $CDCl_3$) 1.38 (12H, s, CH_3), 4.15 (4H, s, OCH_2), 8.78 (1H, t, *J* 1.5, Ar, 2-H), 8.82 (2H, d, *J* 1.5, Ar, 4- and 6-H); $^{13}C\{^1H\}$ NMR (δ; 100 MHz, $CDCl_3$) 28.3 (CH_3), 68.3 ($C(CH)_3)_3$), 79.7 (OCH_2), 125.2 (Ar, 4- and 6-C), 130.3 (Ar, 1- and 3-C), 133.3 (Ar, 2-C), 148.3 (Ar, 5-C), 159.6 (*C*═N); MS (*m*/*z*; ES) 318 (M + H, 100%); high-resolution MS (*m*/*z*, ES), found for M + H 318.1453; $C_{16}H_{20}N_3O_4$ requires 318.1454.

Synthesis of 2,6-Bis(4′,4′-dimethyl-2′-oxazolinyl)phenylchloroplatinum(II), 6a. Method 1. 5a (0.220 g, 0.81 mmol) and potassium tetrachloroplatinate (0.400 g, 0.96 mmol) were refluxed in dried acetic acid (40 mL). Solvent was removed in vacuo, and the residue was taken up in dichloromethane and filtered through a short column containing a layer of Celite and a layer of silica, eluting with more dichloromethane. The solvent was removed in vacuo to give **6a** as a yellow crystalline solid (0.197 g, 49% yield, based on **5a**). **Method 2. 5a** (0.081 g, 0.30 mmol) and potassium tetrachloroplatinate (0.150 g, 0.36 mmol) were refluxed in distilled water (10 mL) for 48 h, and the mixture was not protected from the atmosphere. The black reaction mixture was filtered through Celite, eluting with ethyl acetate, and the solvent removed in vacuo. The yellow residue was purified by column chromatography (5% ethyl acetate/dichloromethane). Solvent was removed in vacuo to give **6a** as a yellow crystalline solid (0.026 g, 17% yield, based on **5a**). Mp: 224 °C dec. Anal. Found: C, 38.18; H, 3.85; N, 5.40. Calcd for $C_{16}H_{19}ClN_2O_2Pt$: C, 38.29; H, 3.82; N, 5.58. IR (ν_{max}; CH_2Cl_2) cm^{-1} 1609 (C═N) cm^{-1}; ^1H NMR (δ; 250 MHz, $CDCl_3$) 1.70 (12H, s, CH_3), 4.58 (4H, s, CH_2), 7.16 (1H, dd, *J* 7.0 and 8.2, Ar, 4-H), 7.36 (2H, (66%) d, *J* 7.2, (34%) app t, $^4J_{PtH}$ 5.9, Ar, 3- and 5-H); ^1H NMR (δ; 250 MHz, d_6-acetone) 1.62 (12H, s, CH_3), 4.73 (4H, s, CH_2), 7.39 (1H, dd, *J* 6.9 and 8.2, Ar, 4-H), 7.42 (2H, (66%) d, *J* 7.4, (34%) app t, $^4J_{PtH}$ 7.5, Ar, 3- and 5-H); $^{13}C\{^1H\}$ NMR (δ; 68 MHz, $CDCl_3$) 25.7 (CH_3), 64.4 ((34%) d, $^2J_{PtC}$ 33, N$C(CH_3)_2$), 81.9 ((34%) d, $^3J_{PtC}$ 26, OCH_2), 120.3 (Ar 4-C), 125.2 ((34%) d, $^3J_{PtC}$ 41, Ar, 3- and 5-C), 126.4 ((34%) d, $^2J_{PtC}$ 40, Ar, 2- and 6-C), 159.0 ((34%) d, $^1J_{PtC}$ 775, Ar 1-C), 175.7 ((34%) d, $^2J_{PtC}$ 194, *C*═N); MS (*m*/*z*; FAB) 502 (M^+, 14%), 466 ($M^+ - Cl$, 100%).

Synthesis of 4-Nitro-2,6-bis(4′,4′-dimethyl-2′-oxazolinyl)phenylchloroplatinum(II), 6b. 5b (1.602 g, 5.05 mmol) and potassium tetrachloroplatinate (2.520 g, 6.07 mmol) were refluxed under nitrogen in dried glacial acetic acid (150 mL). Solvent was removed in vacuo and the black residue purified by column chromatography (dichloromethane). The volume of solvent was reduced in vacuo to approximately 5 mL, and a yellow solid was precipitate by addition of hexane (70 mL). The solvent was decanted and the residue further triturated with hexane (1 × 50 mL) and dried in vacuo to give **6b** as a yellow solid (0.290 g, 11% yield, based on **5b**). Crystals suitable for XRD analysis were obtained by layering a solution of **6b** in dichloromethane with hexane. Mp: 250 °C dec. Anal. Found: C, 35.50; H, 3.44; N, 7.67. Calcd for $C_{16}H_{18}ClN_3O_4Pt$: C, 35.14; H, 3.32; N, 7.68. IR (ν_{max}; CH_2Cl_2) 1607 (C═N) 1547 (NO_2), cm^{-1}; ^1H NMR (δ; 270 MHz, $CDCl_3$) 1.72 (12H, s, CH_3), 4.65 (4H, s, OCH_2), 8.25 (2H, s, Ar, 3- and 5-H); ^1H NMR (δ; 270 MHz, d_6-acetone) 1.74 (12H, s, CH_3), 4.86 (4H, s, OCH_2), 8.30 (2H, s, Ar, 3- and 5-H); $^{13}C\{^1H\}$ NMR (δ; 63 MHz, $CDCl_3$) 27.7 (CH_3), 67.2 ((34%) d, $^2J_{PtC}$ 33.8, N$C(CH_3)_2$), 84.3 ((34%) d, $^3J_{PtC}$ 25.6, OCH_2), 122.87 ((34%) d, $^3J_{PtC}$ 42.7, Ar, 3- and 5-C), 128.7 ((34%) d, $^2J_{PtC}$ 119.1, Ar, 2- and 6-C), 143.2 (Ar, 4-C), 167.7 (Ar, 1-C, $^1J_{PtC}$ coupling not observed), 176.6 (*C*═N, $^2J_{PtC}$ coupling not observed); MS (*m*/*z*; ES) 511 ($M^+ - Cl$, 3%), 552 ($M - Cl + CH_3CN$, 100%); high-resolution MS (*m*/*z*, ES), found for M − Cl + CH_3CN 552.1236; $C_{18}H_{21}N_4O_4Pt$ requires 552.1211.

Synthesis of 2,6-Bis(4′,4′-dimethyl-2′-oxazolinyl)phenylbromopalladium(II), 6c. 5a (0.115 g, 0.42 mmol) and palladium acetate (0.095 g, 0.42 mmol) were refluxed under nitrogen in dried acetic acid (50 mL). Acetic acid was removed in vacuo, and the residue dissolved in chloroform (100 mL). Lithium bromide (0.040 g, 0.46 mmol) was added and the mixture stirred at reflux under nitrogen for 24 h. The cooled residue was filtered and dried in vacuo to give an off-yellow amorphous solid. Initial investigation by ^1H NMR suggested the presence of **7** and **6c** and other organic components. The residue was purified by column chromatography (dichloromethane) to give **6c** as a yellow solid still impure by ^1H NMR (0.005 g, ca. 3% yield): ^1H NMR (δ; 200 MHz, $CDCl_3$) 1.63 (12H, s, CH_3), 4.41 (4H, s, CH_2), 7.12 (1H, app dd, *J* 6.4 and 7.8, Ar, 4-H), 7.25 (2H, d, *J* 7.3, Ar, 3- and 5-H). The ^1H NMR spectrum is consistent with that previously reported.[2f]

Synthesis of Di(2-methyl-2-*N*-acetyl)propyl Isophthalate, 7. 5a (0.112 g, 0.41 mmol) was refluxed in glacial acetic acid (10 mL) for 48 h. Solvent was removed in vacuo to give crude **7** as a colorless solid (0.147 g, 91% yield). A sample for analysis was prepared by recrystallization from methanol/hexane. Mp: 84 °C. Anal. Found: C, 60.91; H, 7.24; N, 7.13. Calcd for $C_{20}H_{28}N_2O_6$: C, 61.21; H, 7.19; N, 7.14. IR (ν_{max}; thin film) 3066 (NH), 1741 (C═O), 1650 (C═O) cm^{-1}; ^1H NMR (δ; 270 MHz, $CDCl_3$) 1.32 (12H, s, C($CH_3)_2$), 2.00 (6H, s, OCCH_3), 4.21 (4H, s, CH_2), 6.61 (2H, s, NH), 7.33 (1H, t, *J* 7.7, Ar, 5-H), 7.75 (2H, app dd, *J* 1.6 and 7.8, Ar, 4- and 6-H), 7.97 (1H, s, Ar, 2-H); $^{13}C\{^1H\}$ NMR (δ; 100 MHz, $CDCl_3$) 20.7 (OCCH_3), 23.7 (C($CH_3)_2$), 53.9 (OCH_2), 69.3 (NH$C(CH_3)_2$), 124.8 (Ar, 5-C), 128.6 (Ar, 4- and 6-C), 129.6 (Ar, 2-C), 135.3 (Ar, 1- and 3-C) 166.1 (CO_2), 171.3 (CH_3CON); MS (*m*/*z*; ES) 393 (M + H, 100%); high-resolution MS (*m*/*z*, ES), found for M + H 393.2025; $C_{20}H_{29}N_2O_6$ requires 393.2026.

Synthesis of 2,6-Bis(4′,4′-dimethyl-2′-oxazolinyl)phenylaquoplatinum(II) Triflate, 15a. 6a (0.10 g, 0.2 mmol) and silver triflate (0.065 g, 0.25 mmol) were stirred in acetone (20 mL) for 24 h protected from light. The reaction mixture was filtered through Celite, eluting with acetone, to remove a gray/white precipitate, consistent with the formation of silver chloride, and dried in vacuo to give **15a** as a pale yellow solid (0.13 g, >99% yield, based on **6a**). Mp: 260 °C dec. IR (ν_{max}; thin film) 3436 (OH), 1643 (C═N), 1336 (SO_3), 1229 (CF_3), 1148 (CF_3), 1034 (SO_3) cm^{-1}; ^1H NMR (δ; 270 MHz, d_6-acetone) 1.48 (12H, s, CH_3), 3.20 (2H, brs, OH_2), 4.82 (4H, s, OCH_2), 7.34 (1H, dd, *J* 6.9 and 8.6, Ar, 4-H), 7.46 (2H, (66%) d, *J* 8.2, (34%) app t, $^4J_{PtH}$ 7.4, Ar, 3- and 5-H); $^{13}C\{^1H\}$ NMR (δ; 63 MHz, d_6-acetone) 27.0 (CH_3), 66.1 ((34%) d, $^2J_{PtC}$ 31.0, N$C(CH_3)_2$), 84.1 ((34%) d, $^3J_{PtC}$ 26, OCH_2), 125.0 (Ar, 4-C), 128.3 ((34%) d, $^3J_{PtC}$ 44.5, Ar, 3- and 5-C), 129.5 ((34%) d, $^2J_{PtC}$ 46.2, Ar, 2- and 6-C), 178.3 (*C*═N, $^2J_{PtC}$ not observed), 1-C and CF_3 not observrd; high-resolution MS (*m*/*z*, ES), found for M − OTf = 466.1094; $C_{16}H_{19}N_2O_2Pt$ requires 466.1089.

Synthesis of 2,6-Bis(4′,4′-dimethyl-2′-oxazolinyl)phenylaquoplatinum(II) Hexafluoroantimonate, 15b. 6a (0.081 g, 0.16 mmol) and silver hexafluoroantimonate (0.08 g, 0.23 mmol) were stirred in acetone (20 mL) for 24 h protected from light. The reaction mixture was filtered through Celite, eluting with acetone, to remove a gray/white precipitate, consistent with the formation of silver chloride, and dried in vacuo to give **15b** as a yellow solid (0.115 g, 99% yield, based on **6a**). This amorphous solid is hydroscopic and discolors within a week in ambient conditions. Mp: 172 °C dec. IR (ν_{max}; thin film) 3436 (OH), 1633 (C═N) cm^{-1}; ^1H NMR (δ; 270 MHz, d_6-acetone) 1.43 (12H, s, CH_3), 2.60−3.4 (2H, brs, OH_2), 4.87 (4H, s, OCH_2), 7.38 (1H, dd, *J* 6.7 and 8.4, Ar, 4-H), 7.51 (2H, (66%) d, *J* 8.4, (34%) app t, $^4J_{PtH}$ 8.3, Ar, 3- and 5-H); $^{13}C\{^1H\}$ NMR (δ; 68 MHz, d_6-acetone) 26.2 (CH_3), 65.6 (N$C(CH_3)_2$), 83.2 (OCH_2), 124.9 (Ar, 4-C), 127.8 ((34%) d, $^3J_{PtC}$ 47.6, Ar, 3- and 5-C), 128.5 (Ar, 2- and 6-C, $^2J_{PtC}$ coupling not observed), 160.1 (Ar, C-1, $^1J_{PtC}$ coupling not observed), 175.0 ((34%) d, $^2J_{PtC}$ 143,

C═N); high-resolution MS (*m*/*z*, ES), found for M − SbF_6 = 484.1193; $C_{16}H_{21}N_2O_3Pt$ requires 484.1194.

Synthesis of 4-Nitro-2,6-bis(4′,4′-dimethyl-2′-oxazolinyl)phenylaquoplatinum(II) Triflate, 15c. 6b (0.130 g, 0.24 mmol) and silver triflate (0.074 g, 0.29 mmol) were stirred in acetone (25 mL) for 24 h protected from light. The reaction mixture was filtered through Celite, eluting with acetone, to remove a gray/white precipitate, consistent with the formation of silver chloride, and dried in vacuo to give a sticky black solid, which was precipitated from ethyl acetate with diethyl ether to give **15c** as a black powder (0.122 g, 72% yield, based on **6b**). Mp: 286 °C dec. IR (ν_{max}; thin film) 3436 (OH), 1643 (C═N), 1487 (NO_2), 1332 (SO_3), 1262 (CF_3), 1181 (CF_3), 1034 (SO_3) cm^{-1}; ^{1}H NMR (δ; 270 MHz, d_6-acetone) 1.45 (12H, s, CH_3), 4.1−6.1 (2H, brs, OH_2), 4.97 (4H, s, OCH_2), 8.26 (2H, s, Ar, 3- and 5-H); ^{13}C{^{1}H} NMR (δ; 68 MHz, d_6-acetone) 27.0 (*C*H_3), 66.7 ((34%) d, $^2J_{PtC}$ 33, N*C*$(CH_3)_2$), 84.8 ((34%) d, $^3J_{PtC}$ 27, O*C*H_2), 122.8 ((34%) d, $^3J_{PtC}$ 51, Ar, 3- and 5-C), 124.8 ((34%) d, $^2J_{PtC}$ 71, Ar, 2- and 6-C), 130.0 (q, $^1J_{CF}$ 38, *C*F_3), 145.4 (Ar, 4-C), 159.6 (Ar, 1-C, $^1J_{PtC}$ coupling not observed), 177.2 ((34%) d, $^2J_{PtC}$ 222, *C*═N); high-resolution MS (*m*/*z*, ES), found for M − OTf = 529.1048; $C_{16}H_{20}N_3O_5Pt$ requires 529.1051.

Synthesis of 2,6-Bis(4′,4′-dimethyl-2′-oxazolinyl)phenylaquopalladium(II) Triflate, 15d. 6c (0.306 g, 0.67 mmol) was dissolved in acetone (30 mL), to which silver triflate (0.190 g, 0.74 mmol) was added, and stirred for 19 h protected from light. The reaction mixture was filtered through Celite, eluting with acetone, to remove a gray/white precipitate, consistent with the formation of silver bromide. The solvent was removed in vacuo and the residue triturated with hexane to give previously reported **15d**[2f] as an off-white solid (0.19 g, 52% yield based on **6c**). Mp: 254 °C dec. Anal. Found: C, 37.62; H, 4.00; N, 5.00. Calcd for $C_{17}H_{21}F_3N_2O_6PdS$: C, 37.48; H, 3.88; N, 5.14. IR (ν_{max}; KBr disk) 1620 (C═N), 1302, 1032 (SO_3) cm^{-1}; ^{1}H NMR (δ; 270 MHz, d_6-acetone) 1.43 (12H, s, CH_3), 3.34 (2H, br s, OH_2), 4.70 (4H, s, CH_2), 7.38 (1H, t, *J* 5.8, Ar, 4-H), 7.45 (2H, d, *J* 5.8, Ar, 3- and 5-H); MS (*m*/*z*; FAB) 378 (M^+ − OH_2 − OTf, 100%).

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Supporting Information Available: Details of the X-ray structure determination of **6b** together with data and further details on the determination of the rate constrants given in Tables 1 and 2. This material is available free of charge via the Internet at http://pubs.acs.org.

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