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Stereospecific Synthesis of Polysubstituted *E*-Olefins by Reaction of Acyclic Nitrones with Free and Platinum(II) Coordinated Organonitriles

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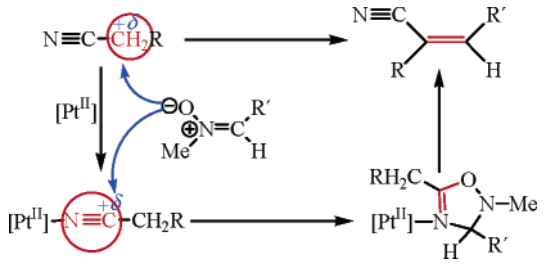

Free nitriles $NCCH_2R$ (**1a** R = CO_2Me, **1b** R = SO_2Ph, and **1c** R = COPh) with an acidic α-methylene react with acyclic nitrones $^{-}O^{+}N(Me)=C(H)R'$ (**2a** R′ = 4-MeC_6H_4 and **2b** R′ = 2,4,6-$Me_3C_6H_2$), in refluxing CH_2Cl_2, to afford stereoselectively the *E*-olefins (NC)(R)C=C(H)R′ (**3a**−**3c** and **3a′**−**3c′**), whereas, when coordinated at the platinum(II) *trans*-$[PtCl_2(NCCH_2R)_2]$ complexes (**4a** R = CO_2Me and **4b** R = Cl), they undergo cycloaddition to give the (oxadiazoline)-Pt^{II} complexes *trans*-$[PtCl_2\{N{=}C(CH_2R)ON(Me)C(H)R'\}_2]$ (R = CO_2Me, Cl and R′ = 4-MeC_6H_4, 2,4,6-$Me_3C_6H_2$) (**5a-5d**). Upon heating in CH_2Cl_2, **5a** affords the corresponding alkene **3a**. The reactions are greatly accelerated when carried out under focused microwave irradiation, particularly in the solid phase (SiO_2), without solvent, a substantial increase of the yields being also observed. The compounds were characterized by IR and ^{1}H, ^{13}C, and ^{195}Pt NMR spectroscopies, FAB^{+}-MS, elemental analyses and, in the cases of the alkene (NC)(CO_2Me)C=C(H)(4-MeC_6H_4) **3a** and of the oxadiazoline complex *trans*-$[PtCl_2\{N{=}C(CH_2Cl)ON(Me)C(H)(4\text{-}C_6H_4Me)\}_2]$ **5c**, also by X-ray diffraction analyses.

Introduction

The stereoselective syntheses of substituted alkenes is an important aim in organic chemistry. The most general approach involves elimination reactions that, however, commonly give rise to a mixture of double bond isomers with eventual predominance of one of them (Zaytzev or Hofmann rules), but a high selectivity is rare.[1] The first powerful methods for the selective synthesis are comprised of the Knoevenagel condensations,[2] the McMurry[3] and Wittig[4] reactions from aldehydes or ketones, which have been shown recently to be accelerated by microwave irradiation.[5] Olefin metathesis provides powerful synthetic tools within both functionalized and unfunctionalized olefins.[6]

Free nitriles are only rarely used for alkene synthesis due to their usually low reactivity, namely, toward most dipolar reagents. One of the first known feasible conversions into an

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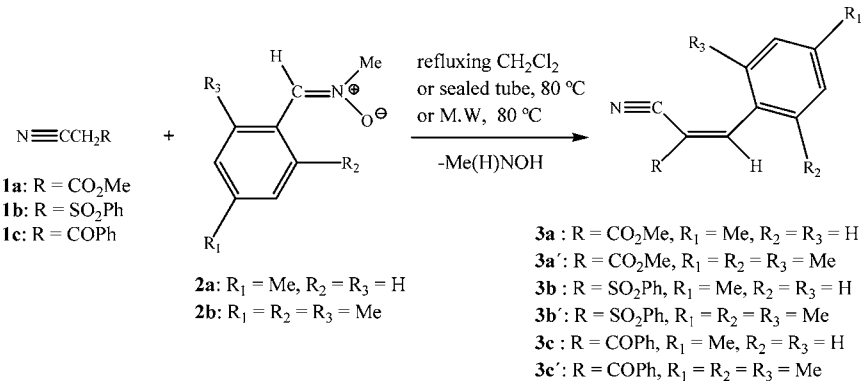
SCHEME 1



olefin (i.e., a cyano-olefin or α,β-unsaturated nitrile) using acidic methylene organonitriles with various types of catalysts, such as $AlPO_4-Al_2O_4$[7a] or $-Al_2O_3$,[7b] was devised by using the Knoevenagel condensation[7] with some carbonyl compounds. Metal catalysts such as Ru^{II} have also been applied to give the same type of olefins.[8] Only activated nitriles RCN, with a strong electron-withdrawing group (e.g., R = CCl_3, CO_2R') directly ligated to the triple bond, react with some dipolar species such as nitrones, unless rather harsh conditions and/or long reaction times are employed.[9] Nitrile coordination to a suitable metal center can also lead to its activation toward a variety of nucleophiles and dipoles.[10] A recent nitrile application in heterocyclic synthesis, unreachable from a free nitrile, achieved in our laboratory, involves the reaction of $NCCH_2R$ (R = CO_2-Me, Cl) at a Pt^{II} center with a cyclic nitrone.[11a] The dipolarophilicity of the triple bond is enhanced by the Pt^{II} site, and the coupling reactions can also be promoted by microwave irradiation.[11c] However, in those reactions, no role of the acidic α-hydrogens in $NCCH_2R$ was recognized.

These results stimulated our interest toward (i) the search for another type of reaction centered at the acidic α-CH_2 group of $NCCH_2R$, (ii) the extension of the studies to acyclic nitrones that are less reactive than the cyclic ones, and (iii) the investigation of the effects on the nitrile reactivity of the electron-acceptor R group and of the nitrile coordination to a Pt^{II} center.

In the first part of this work, we report an unprecedented reaction of free acidic α-CH_2 organonitriles with an electron-withdrawing substituent (R = CO_2Me, SO_2Ph, COPh), with acyclic nitrones, which constitutes a novel and simple alternative method for the preparation of pure unsymmetrical cyano-functionalized *E*-alkenes without the use of any catalyst. In the second part, we examine the reactivity of the Pt^{II}-bound nitriles to form heterocyclic oxadiazoline complexes that can lead to the cyano-alkenes. The reactions are markedly accelerated by microwave (M.W.) irradiation, particularly in the solid phase (SiO_2), which also results in a considerable yield improvement.

Results and Discussion

We have studied the reactions of acyclic nitrones $^-O^+N(Me)$═C(H)R′ **2** (**2a** R′ = 4-MeC_6H_4 and **2b** R′ = 2,4,6-$Me_3C_6H_2$) with various acidic methylene nitriles $NCCH_2R$ **1** bearing an electron-acceptor group (**1a** R = CO_2Me, **1b** R = SO_2Ph, **1c** R = COPh, and **1d** R = Cl) by four different methods (conventional solvent reflux, heating in a sealed tube, and microwave irradiation in CH_2Cl_2 and in the solid phase) (see Experimental Procedures). The corresponding *E*-cyano-alkene products (NC)(R)C═C(H)R′ **3** were isolated by column chromatography and obtained as pale yellow or white solids (Scheme 1).

The reactions are greatly accelerated by focused M.W. irradiation, taking then typically 2 h, whereas conventional heating methods require much longer times (3 or 4 days in refluxing CH_2Cl_2 or 12 h in CH_2Cl_2 heated in a sealed tube at 80 °C).

The highest yields (80−55%, depending on the nitrile substituent) are obtained under M.W. irradiation in the solid phase (SiO_2), without solvent, at 80 °C, while the other methods typically lead only to 56−15% yields. The reactivity of the nitriles follows the electron-withdrawing ability of the R substituent (i.e., SO_2Ph > CO_2Me > COPh > Cl), with $NCCH_2$-SO_2Ph as the more reactive nitrile, whereas no trace of olefin was detected in the case of $NCCH_2Cl$. Hence, the reactions are quite sensitive to the nature of the nitrile substituent.

The formation of the *E*-alkene products **3** involves the overall and formal removal of the two acidic methylene protons of the

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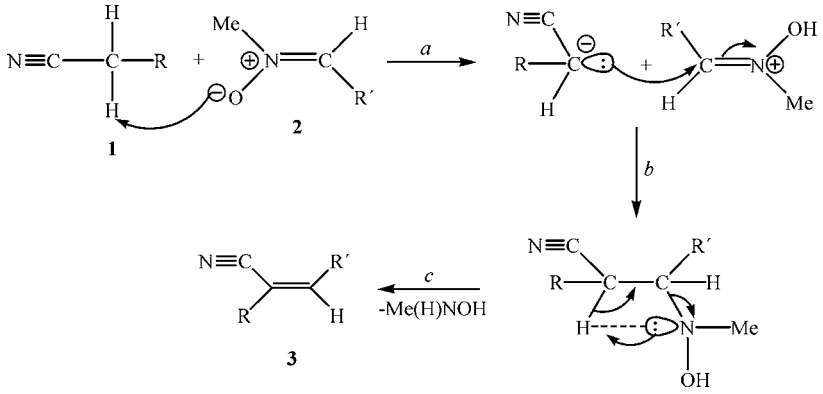
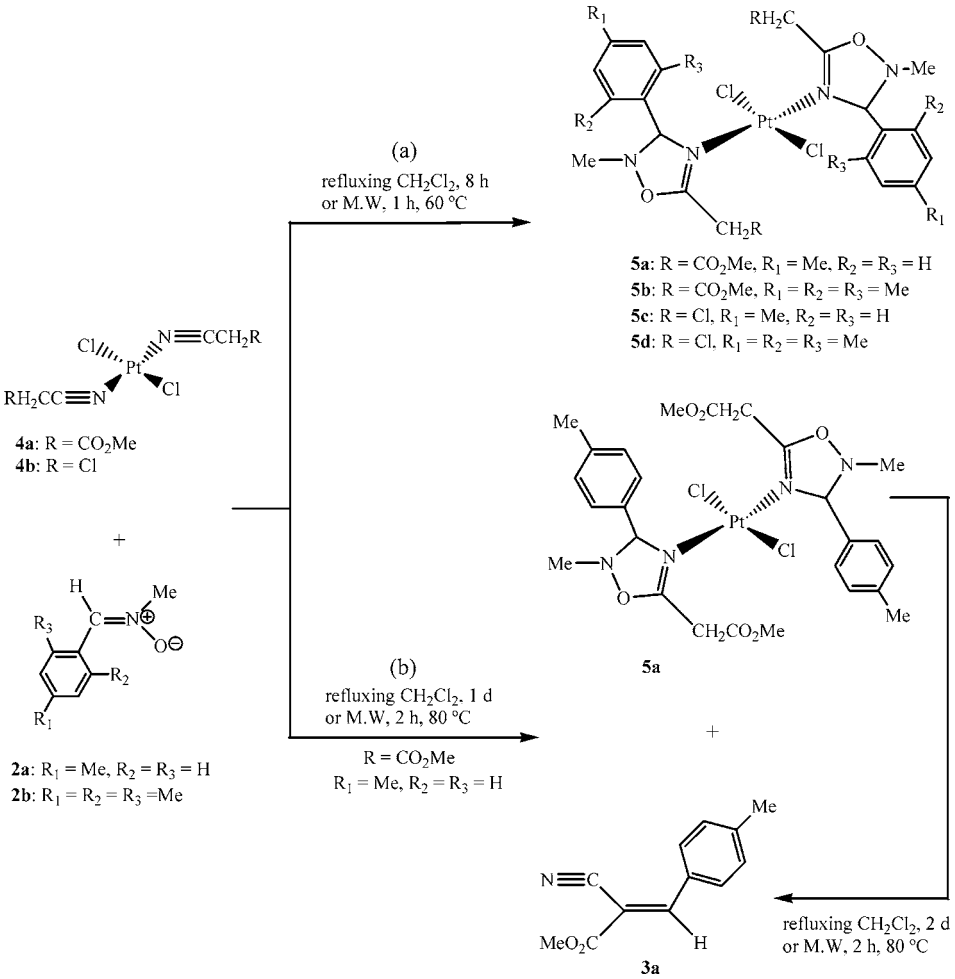
SCHEME 2



nitrile $NCCH_2R$ by the $\{NOMe\}^{2-}$ fragment of the nitrone $^{-}O^{+}N(Me)=C(H)R'$, which thus undergoes N=C bond cleavage, with coupling of the remaining nitrile- and oxime-derived fragments to afford (NC)(R)C=C(H)R′. This unprecedented type of reaction is determined by the acidic character of the α-protons of the nitrile, which exhibit a higher reactivity than the cyano group that remains unreactive. A conceivable mechanism is proposed in Scheme 2. The reaction is initiated by single deprotonation of the nitrile $NCCH_2R$ by the nitrone (step a) to give the anionic basic form of the former (i.e., $NCCHR^{-}$), which upon nucleophilic attack at the $C=N^{+}$ carbon of the cationic protonated nitrone (step b) forms a cyano-alkylhydroxylamine intermediate. Abstraction of the second proton from the cyano-alkyl fragment by the amine nitrogen with concomitant C=C bond formation and C−N bond cleavage leads (step c) to the elimination of hydroxylmethylamine Me(H)NOH and the corresponding cyano-alkene (NC)(R)C=C(H)R′ **3**.

The cyano-alkene products **3** were characterized by IR, ^{1}H and ^{13}C NMR spectroscopies, FAB^{+}-MS, elemental analyses, and (for **3a**) single-crystal X-ray diffraction. In the IR spectra of **3**, $\nu(N\equiv C)$ appears in the same range of wavenumbers as that observed for the starting nitriles (2214−2225 cm^{-1}), while the detection of new bands at 1595−1611 cm^{-1} assigned to $\nu(C=C)$ confirms the formation of the alkenes. In ^{1}H NMR

SCHEME 3



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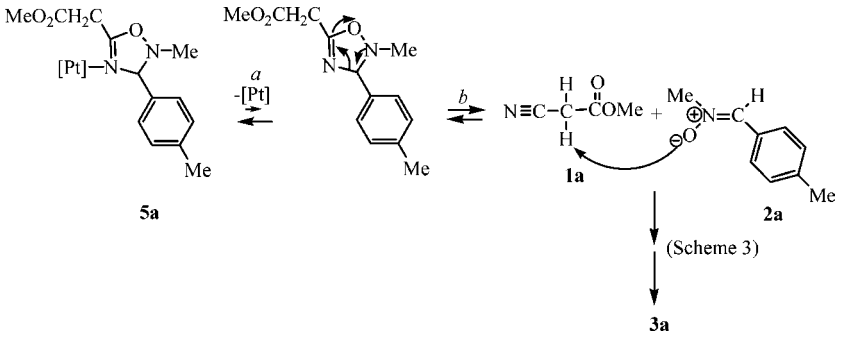


spectra, the C═CH resonance is detected at δ 8.06−8.51, and the protons of the methyl groups at the aromatic rings appear in the 2.22−2.46 ppm range. In the $^{13}C\{^1H\}$ NMR spectra, the signals of the C═C carbons emerge in intervals from 101.5 to 116.4 and 152.2 to 158.9 ppm, while the carbons of the N≡C groups are observed in the 114.0−122.3 ppm range.

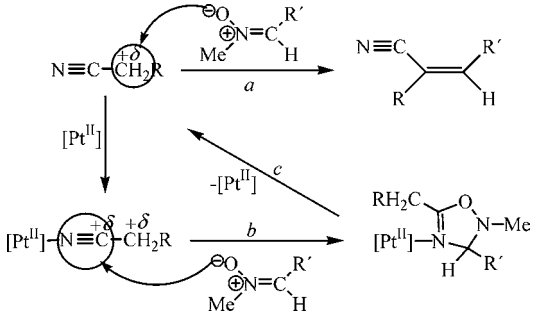
The single-crystal X-ray diffraction analysis of (NC)(CO_2Me)C═C(H)(4-MeC_6H_4) **3a** (see the Supporting Information) confirms the *E* configuration. The cyano-C(4)≡N(1) triple bond length, 1.149 Å, and the alkene double bond C(3)═C(5) distance, 1.349 Å, are in accord with the reported[12] average values of 1.144 and 1.340 Å, respectively.

In the second part of this work, we investigated the reactions of the nitriles with the nitrones after coordination of the former to a Pt^{II} center, thus comparing the reactivities of the ligated and free nitriles and studying the metal activating effect. Treatment of *trans*-[$PtCl_2$(NCCH_2R)$_2$] (**4a** R = CO_2Me and **4b** R = Cl) with $^-O^+$N(Me)═C(H)R′ (**2a** R′ = 4-MeC_6H_4 and **2b** R′ = 2,4,6-$Me_3C_6H_2$) upon heating (8 h, refluxing CH_2Cl_2) gives a 1:1 diastereomeric mixture of the corresponding (Δ^4-1,2,4-oxadiazoline)-Pt^{II} complexes *trans*-[$PtCl_2${N═C(CH_2R)ON(Me)C(H)R′}$_2$] **5a**−**d** in moderate yields (58−53%) (Scheme 3 a). The reaction time is drastically reduced with M.W. irradiation (1 h, 60 °C) giving complexes **5** in comparable yields (60−55%).

These reactions allowed the direct synthesis of new oxadiazoline−Pt^{II} complexes from nitrile Pt^{II} precursors upon nitrile/nitrone coupling ([2 + 3] cycloaddition). The coordination of the nitrile NCCH_2R to the Pt^{II} center activates the cyano group to such an extent that it becomes more reactive toward the nitrone than the acidic methylene moiety, in contrast to what we have observed for the free nitrile. The oxadiazoline complexes **5a**−**d** have been characterized by IR, ^1H, ^{13}C, and ^{195}Pt NMR spectroscopies (data are in accord with those of other oxadiazoline complexes[11b,13−16]), FAB^+-MS, elemental analyses, and (for **5c**) single-crystal X-ray diffraction (see Supporting Information). All bond lengths and angles are normal and agree with those reported[13,14] for other oxadiazoline−Pt complexes.

Interestingly, the oxadiazoline−Pt^{II} complex **5a** leads to the corresponding cyano-alkene **3a** [Scheme 3b]. In fact, if the reaction of *trans*-[$PtCl_2$(NCCH_2CO_2Me)$_2$] **4a** with **2a** is undertaken under more drastic conditions (1 day in refluxing CH_2Cl_2 or 2 h under M.W. irradiation at 80 °C) than those normally used, we obtain a mixture of **5a** and the cyano-alkene **3a**. Moreover, refluxing a CH_2Cl_2 solution of **5a** for 2 days or heating it for 2 h under M.W. irradiation at 80 °C leads to the cyano-alkene **3a**. These results suggest that the formation of an oxadiazoline complex via [2 + 3] cycloaddition of the nitrone with a ligated nitrile can be kinetically driven and that such a complex, upon prolonged reaction time and at a higher temperature, can convert into the thermodynamically more stable cyano-alkene product. A possible pathway for the conversion of the oxadiazoline complex **5a** into the corresponding alkene **3a** is proposed in Scheme 4, involving a retrocycloaddition process. Liberation (even only to a slight extent) of the oxadiazoline ligand (step a) and dissociation of this species into the starting nitrile and nitrone components (step b) would be followed by proton abstraction from the methylene group of the nitrile by the nitrone.

SCHEME 5



Conclusion

Organonitriles bearing an acidic α-methylene group, NCCH_2R (R = electron-withdrawing group), exhibit two reactive centers (i.e., the CH_2 and the cyano moieties). In the absence of a coordinating metal site, the methylene group is more reactive than the cyano center toward an acyclic nitrone, undergoing deprotonation by the latter reagent to provide a simple and novel stereoselective synthetic route for polysubstituted *E*-alkenes (cyano-alkenes) (Scheme 5, route a). However, upon binding a Pt^{II} Lewis acid site, the cyano group of the nitrile becomes more reactive than the methylene group, being thus sufficiently activated by coordination to undergo a [2 + 3] cycloaddition with the acyclic nitrone to afford oxadiazoline complexes (Scheme 5, route b) that can be isolated without undergoing ring opening by N−O bond rupture, in contrast to what we have previously observed[11a] for the case of the more reactive cyclic

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nitrones. Nevertheless, an oxadiazoline complex can react further, corresponding to a kinetically favored product that, upon ligand liberation and retrocycloaddition (Scheme 5, route c), generates also the cyano-alkene (route *a*) and Me(H)NOH as the final thermodynamically favored products.

The reactions are greatly accelerated by microwave irradiation, and in particular, the novel route a to the cyano-alkenes thus proceeds in a considerably short reaction time (2 h) and, when performed in the solid phase (SiO_2), displays moderate to good yields (up to 80%) thus providing a contribution toward an environmentally friendly process with potential significance in green chemistry. Other advantages of route a to polysubstituted *E*-alkenes include its simplicity, its stereoselectivity, the possibility of extension to a variety of substituted alkenes (NC)-(R)C═C(H)R′ simply by varying the electron-acceptor R group and R′ of the starting nitrile and nitrone, respectively, the use of easily available starting materials, and that it is not necessary to apply any catalyst or promoter.

As a final comment, the new oxadiazoline complexes with ester or chloro substituents are expected to be potential precursors for the synthesis of aminoacids and lactams[17] and eventually can also exhibit anticancer activity (as other platinum complexes with *N*-heterocyclic ligands),[18] aspects that are currently under consideration in our group.

Experimental Procedures

The organonitrile complexes *trans*-[$PtCl_2(NCCH_2R)_2$] (**4a** R = CO_2Me and **4b** R = Cl)[11a] and the nitrones **2a**[19] and **2b**[19] were prepared according to published methods.

Syntheses. The heating methods used are as follows. (i) Conventional method: the reaction was carried out in refluxing CH_2Cl_2 with stirring, and its progress was monitored by TLC. After evaporation of the solvent in vacuo to dryness, the crude residue was purified by column chromatography on silica (CH_2Cl_2 as the eluent) followed by evaporation of the solvent in vacuo to give the final yellow or white solids. (ii) In a sealed tube: the reagents were heated in a sealed stainless steel tube (20 mL), and the progress of the reaction was monitored by TLC. After evaporation of the solvent in vacuo to dryness, the crude residue was purified as indicated in (i). (iii) By focused microwave irradiation in solution: the reagents and solvent (CH_2Cl_2) were added to a cylindrical Pyrex tube that was then placed in a focused microwave CEM Discover reactor (10 mL, 13 mm diameter, 300 W), which was fitted with a rotational system and an IR detector of temperature. After the reaction, the mixture was allowed to cool down, the solvent was removed in vacuo, and the crude residue was purified as indicated in (i). (iv) By focused microwave irradiation in the solid phase: the reagents and the silica (SiO_2) support were placed in a cylindrical Pyrex tube, and the mixture was impregnated with CH_2Cl_2; after subsequent solvent removal, the system was placed in the microwave reactor and irradiated at 80 °C for 2 h. The crude product was purified by column chromatography on silica with CH_2Cl_2 as the eluent, as indicated previously.

Reaction of Free Nitriles $NCCH_2R$ (1a R = CO_2Me, 1b R = SO_2Ph, and 1c R = COPh) with Acyclic Nitrones $^-O^+N(Me)$═C(H)R′ (2a R′ = 4-MeC_6H_4 and 2b R′ = 2,4,6-$Me_3C_6H_4$).

(i) By the conventional method: a solution of **1a** (60.0 mg, 0.605 mmol), or **1b** (60.0 mg, 0.331 mmol), or **1c** (60.0 mg, 0.413 mmol) in dry CH_2Cl_2 (3.0 mL) was added at room temperature to the appropriate nitrone **2** (1.2 equiv), and the mixture was heated to reflux with stirring for 3 or 4 days. (ii) In a sealed tube: the reagents, in amounts identical to those detailed previously, were heated at 80 °C in a sealed tube for 12 h. (iii) By focused microwave irradiation in CH_2Cl_2: the CH_2Cl_2 solution of the reagents in the previous amounts was subject to microwave irradiation at 80 °C for 2 h. (iv) By focused microwave irradiation onto silica gel support: the previous amounts of reagents were mixed with SiO_2 (1 g), and CH_2Cl_2 (1 mL) was used for impregnation; after solvent evaporation in vacuo, the dried solid mixture was heated at 80 °C under microwave irradiation for 2 h. In all cases, the corresponding cyano-alkenes **3** were isolated and purified as indicated previously, as yellow or white hygroscopic solids.

Methyl (*E*)-2-Cyano-3-(4-methylphenyl)-2-propenoate (3a). Method (i) (30% yield), method (ii) (51% yield), method (iii) (35% yield), and method (iv) (71% yield). TLC on SiO_2: R_f = 0.71 (eluent CH_2Cl_2). Mp: 92 °C. IR (cm^{-1}): 2222 (N≡C), 1728 (CO_2-Me), 1599 (C═C). ^1H NMR ($CDCl_3$), δ: 2.45 (s, 3H, CH_3Ph), 3.94 (s, 3H, CH_3O), 7.32 (d, J_{HH} 8.1 Hz, 2H), 7.91 (d, J_{HH} 8.1 Hz, 2H), 8.24 (s, 1H, C*H*). $^{13}C\{^1H\}$ NMR ($CDCl_3$), δ: 22.5 (*C*H_3Ph), 53.9 (*C*H_3O), 102.1 (*C* = C), 116.5 (N≡*C*), 129.5 and 130.8, 132.0 and 145.5 ($C_{aromatic}$), 156.0 (*C*═*C*), 164.1 (*C*═O). FAB$^+$-MS, *m*/*z*: 201 $[M]^+$. Anal. Calcd for $C_{12}H_{11}NO_2$: C, 71.6; H, 5.5; N, 6.9. Found: C, 71.7; H, 5.7; N, 6.8.

Methyl (*E*)-2-Cyano-3-mesityl-2-propenoate (3a′). Method (i) (33% yield), method (ii) (52% yield), method (iii) (36% yield), and method (iv) (61% yield). TLC on SiO_2: R_f = 0.86 (eluent CH_2Cl_2). Mp: 102 °C. IR (cm^{-1}): 2225 (N≡C), 1735 (CO_2Me), 1611 (C═C). ^1H NMR ($CDCl_3$), δ: 2.29 and 2.31 (two s, 9H, CH_3Ph), 3.95 (s, 3H, CH_3O), 6.93 (s, 2H, Ph), 8.50 (s, 1H, C*H*). $^{13}C\{^1H\}$ NMR ($CDCl_3$), δ: 20.9 and 21.8 (*C*H_3Ph), 54.0 (*C*H_3O), 111.0 (*C*═C), 115.0 (N≡*C*), 129.7, 130.3, 136.8, and 140.9 ($C_{aromatic}$), 158.9 (*C*═*C*), 162.7 (*C*═O). FAB$^+$-MS, *m*/*z*: 230 $[M + 1]^+$. Anal. Calcd for $C_{14}H_{15}NO_2$: C, 73.3; H, 6.6; N, 6.1. Found: C, 73.1; H, 6.7; N, 6.2.

(*E*)-2-(4-Methylphenyl)-1-phenylsulfonyl-1-ethenyl Cyanide (3b). Method (i) (40% yield), method (ii) (56% yield), method (iii) (42% yield), and method (iv) (80% yield). TLC on SiO_2: R_f = 0.83 (eluent CH_2Cl_2). Mp: 146 °C. IR (cm^{-1}): 2218 (N≡C), 1595 (C═C). ^1H NMR ($CDCl_3$), δ: 2.45 (s, 3H, CH_3Ph), 7.28−8.02 (m, 9H), 8.21 (s, 1H, C*H*). $^{13}C\{^1H\}$ NMR ($CDCl_3$), δ: 22.6 (*C*H_3Ph), 101.5 (*C*═C), 114.0 (N≡*C*), 128.3, 129.3, 130.3, 130.9, 131.9, 135.2, 138.9, and 146.4 ($C_{aromatic}$), 152.2 (*C* = *C*). FAB$^+$-MS, m/z: 284 $[M+1]^+$. Anal. Calcd for $C_{16}H_{13}NO_2S$: C, 67.8; H, 4.6; N, 4.9. Found: C, 68.0; H, 4.7; N, 4.9.

(*E*)-2-Mesityl-1-phenylsulfonyl-1-ethenyl Cyanide (3b′). Method (i) (38% yield), method (ii) (54% yield), method (iii) (41% yield), and method (iv) (75% yield). TLC on SiO_2: R_f = 0.84 (eluent CH_2Cl_2). Mp: 102 °C. IR (cm^{-1}): 2225 (N≡C), 1602 (C═C). ^1H NMR ($CDCl_3$), δ: 2.22 and 2.28 (two s, 9H, CH_3Ph), 6.91 (s, 2H, $Me_3C_6H_2$), 7.61−7.76 (m, 3H, Ph), 8.04 (d, J_{HH} 7.8 Hz, 2H, Ph), 8.51 (s, 1H, C*H*). $^{13}C\{^1H\}$ NMR ($CDCl_3$), δ: 20.7 and 21.8 (*C*H_3-Ph), 112.7 (*C*═C), 122.3 (N≡*C*), 129.1, 129.7, 129.8, 130.4, 135.4, 136.9, 138.4, and 141.5 ($C_{aromatic}$), 155.2 (*C*═*C*). FAB$^+$-MS, *m*/*z*: 312 $[M + 1]^+$. Anal. Calcd for $C_{18}H_{17}NO_2S$: C, 69.4; H, 5.5; N, 4.5. Found: C, 69.3; H, 5.7; N, 4.3.

(*E*)-1-Benzoyl-2-(4-methylphenyl)-1-ethenyl Cyanide (3c). Method (i) (17% yield), method (ii) (48% yield), method (iii) (35% yield), and method (iv) (56% yield). TLC on SiO_2: R_f = 0.76 (eluent CH_2Cl_2). Mp: 90 °C. IR (cm^{-1}): 2214 (N≡C), 1668 (C═O), 1596 (C═C). ^1H NMR ($CDCl_3$), δ: 2.46 (s, 3H, CH_3Ph), 7.32−7.97 (m, 9H, Ph), 8.06 (s, 1H, C*H*). $^{13}C\{^1H\}$ NMR ($CDCl_3$), δ: 22.6 (*C*H_3Ph), 109.6 (*C* = C), 118.1 (N≡*C*), 129.3, 129.9, 130.8, 132.05, 133.9, 136.8, 137.0, and 145.5 ($C_{aromatic}$), 156.3 (*C*═*C*),

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193.9 (*C*═O). FAB$^+$-MS, *m*/*z*: 248 [M + 1]$^+$. Anal. Calcd for $C_{17}H_{13}NO$: C, 82.6; H, 5.3; N, 5.7. Found: C, 82.6; H, 5.0; N, 5.7.

(*E*)-1-Benzoyl-2-mesityl-1-ethenyl Cyanide (3c′). Hygroscopic compound becomes a viscous oil in air at room temperature but remains a solid compound under a dinitrogen atmosphere. Method (i) (15% yield), method (ii) (47% yield), method (iii) (38% yield), and method (iv) (55% yield). TLC on SiO_2: R_f = 0.87 (eluent CH_2Cl_2). IR (cm^{-1}): 2218 (N≡C), 1668 (C═O), 1597 (C═C). ^{1}H NMR ($CDCl_3$), δ: 2.34 and 2.36 (two s, 9H, C*H*$_3$Ph), 6.98 (s, 2H, $Me_3C_6H_2$), 7.54−7.69 (m, 3H, Ph), 7.95 (d, J_{HH} 7.5 Hz, 2H, Ph), 8.29 (s, 1H, C*H*). ^{13}C{^{1}H} NMR ($CDCl_3$), δ: 21.1 and 21.8 (*C*H$_3$Ph), 116.4 (*C*═C), 118.5 (N≡*C*), 129.4, 129.6, 129.7, 130.0, 134.4, 136.2, 136.7, and 140.8 ($C_{aromatic}$), 158.8 (*C*═*C*), 188.7 (*C*═O). FAB$^+$-MS, *m*/*z*: 276 [M + 1]$^+$. Anal. Calcd for $C_{19}H_{17}NO\bullet 3/2\ H_2O$: C, 69.3; H, 7.0; N, 4.2. Found: C, 69.5; H, 6.9; N, 4.0.

Reactions of Organonitrile Platinum(II) Complexes *trans*-[$PtCl_2(NCCH_2R)_2$] (4a R = CO_2Me and 4b R = Cl) with Acyclic Nitrones $^-O^+N(Me)$═C(H)(R′) (2a R′ = 4-MeC_6H_4 and 2b R′ = 2,4,6-$Me_3C_6H_2$). A solution of **4a** (50.0 mg, 0.107 mmol) or **4b** (50.0 mg, 0.119 mmol) in dry CH_2Cl_2 (3.0 mL) was added at room temperature to the nitrones **2a** or **2b** (2.2 equiv). The mixture was heated to reflux with stirring for 8 h, and a bright yellow solution was formed. The progress of the reaction was monitored by TLC. After evaporation of the solvent in vacuo to dryness, the crude residue was purified by column chromatography (SiO_2/CH_2Cl_2, Et_2O) followed by evaporation of the solvent in vacuo to dryness to give a yellow powder of the corresponding final oxadiazoline complex **5** (two diastereoisomers; distinct δ values are indicated below when the resonances are resolved). The reaction is greatly accelerated with microwave irradiation (1 h, 60 °C) to give the products in yields (60−55%) that are comparable to those (58−53%) obtained in conventional refluxing CH_2Cl_2.

***trans*-[$PtCl_2${N═C(CH_2CO_2Me)ON(Me)C(H)(4-MeC_6H_4)}$_2$] (5a).** Yield: 57%. TLC on SiO_2: R_f = 0.64 (eluent CH_2Cl_2/Et_2O (20:1)). Mp: 182 °C. IR (cm^{-1}): 1749 (C═O), 1657 (C═N). ^{1}H NMR ($CDCl_3$), δ: 2.39 (s, 6H, C*H*$_3$Ph), 2.91 and 2.96 (two s, 6H, CH_3N), 3.77 and 4.46 (m, 10H, C*H*$_2$$CO_2$*Me*), 5.83 (m, 2H, N-C*H*-N), 7.19−7.52 (m, 8H, Ph). ^{13}C{^{1}H} NMR ($CDCl_3$), δ: 22.0 (*C*H$_3$-Ph), 34.3 (*C*H$_3$N), 47.4 (*C*H$_2$), 53.7 (*C*H$_3$O), 92.6 (N-*C*H-N), 128.4, 130.2, 131.1, and 133.1 ($C_{aromatic}$), 160.9 (*C*═N), 165.1 (*C*═O). ^{195}Pt NMR ($CDCl_3$), δ: −2290 (614 Hz). FAB$^+$-MS, *m*/*z*: 762 [M]$^+$. Anal. Calcd for $C_{26}H_{32}N_4O_6Cl_2Pt\bullet 1/2CH_2Cl_2\bullet Et_2O$: C, 41.6; H, 4.9; N, 6.3. Found: C, 41.9; H, 4.7; N, 6.1. The solvents of crystallization CH_2Cl_2 and Et_2O have been detected in the NMR spectra.

***trans*-[$PtCl_2${N═C(CH_2CO_2Me)ON(Me)C(H)(2,4,6-$Me_3C_6H_2$)}$_2$] (5b).** Yield: 56%. TLC on SiO_2: R_f = 0.66 (eluent CH_2Cl_2/Et_2O (20:1)). Mp: 145 °C. IR (cm^{-1}): 1747 (C═O), 1666 (C═N). ^{1}H NMR ($CDCl_3$), δ: 2.30, 2.37, and 2.40 (three s, 18H, C*H*$_3$Ph), 2.88 and 2.90 (two s, 6H, CH_3N), 3.74 and 4.21 (m, 10H, C*H*$_2$$CO_2$*Me*), 6.02 (s, 2H, N−C*H*-N), 6.80 (s, 4H, Ph). ^{13}C{^{1}H} NMR ($CDCl_3$), δ: 20.9 and 21.7 (*C*H$_3$Ph), 34.1 (*C*H$_3$N), 47.8 (*C*H$_2$), 53.5 (*C*H$_3$O), 90.7 (N-*C*H-N), 128.2, 128.5, 130.4, and 139.6 ($C_{aromatic}$), 163.4 (*C*═N), 165.9 (*C*═O). ^{195}Pt NMR ($CDCl_3$), δ: −2221 (926 Hz) and −2254 (806 Hz). FAB$^+$-MS, *m*/*z*: 819 [M]$^+$. Anal. Calcd for $C_{30}H_{40}N_4O_6Cl_2Pt$: C, 44.0; H, 4.9; N, 6.8. Found: C, 44.3; H, 4.5; N, 6.7.

***trans*-[$PtCl_2${N═C(CH_2Cl)ON(Me)C(H)(4-MeC_6H_4)}$_2$] (5c).** Yield: 58%. TLC on SiO_2: R_f = 0.79 (eluent CH_2Cl_2). Mp: 191 °C. IR (cm^{-1}): 1664 (C═N). ^{1}H NMR ($CDCl_3$), δ: 2.39 (s, 6H, C*H*$_3$Ph), 2.92 and 2.93 (two s, 6H, C*H*$_3$N), 4.39 (two d, J_{HH} 13.5, 13.2 Hz, 2H, C*H*$_2$Cl), 4.96 (two d, J_{HH} 13.5, 13.2 Hz, 2H, C*H*$_2$Cl), 5.80 and 5.84 (two s, 2H, N-C*H*-N), 7.18−7.51 (m, 8H, Ph). ^{13}C-{^{1}H} NMR ($CDCl_3$), δ: 22.1 (*C*H$_3$Ph), 34.2 (*C*H$_3$N), 46.7 and 46.8 (*C*H$_2$Cl), 92.9 (N-*C*H-N), 128.6, 130.0, 130.5, and 140.2 ($C_{aromatic}$), 165.5 (*C*═N). ^{195}Pt NMR ($CDCl_3$), δ: −2232 (701 Hz) and −2251 (806 Hz). FAB$^+$-MS, *m*/*z*: 715 [M]$^+$. Anal. Calcd for $C_{22}H_{26}N_4O_2Cl_4Pt$: C, 36.9; H, 3.7; N, 7.8. Found: C, 37.1; H, 4.1; N, 7.7.

***trans*-[$PtCl_2${N═C(CH_2Cl)ON(Me)C(H)(2,4,6-$Me_3C_6H_2$)}$_2$] (5d).** Yield: 53%. TLC on SiO_2: R_f = 0.84 (eluent CH_2Cl_2). Mp: 179 °C. IR (cm^{-1}): 1662 (C═N). ^{1}H NMR ($CDCl_3$), δ: 2.30, 2.36, and 2.39 (three s, 18H, C*H*$_3$Ph), 2.91 and 2.93 (two s, 6H, CH_3N), 4.54 (d, J_{HH} 13.2 Hz, 2H, CH_2Cl), 4.69 (d, J_{HH} 13.2 Hz, 2H, CH_2-Cl), 5.94 and 6.05 (two s, 2H, N-C*H*-N), 6.83 (s, 4H, Ph). ^{13}C-{^{1}H} NMR ($CDCl_3$), δ: 20.6, 20.9 and 21.8 (*C*H$_3$Ph), 34.2 (*C*H$_3$N), 47.7 (*C*H$_2$Cl), 91.4 (N-*C*H−N), 128.0, 128.4, 130.6 and 140.0 ($C_{aromatic}$), 164.7 (*C*═N). ^{195}Pt NMR ($CDCl_3$), δ: −2191 (806 Hz). FAB$^+$-MS, *m*/*z*: 771 [M]$^+$. Anal. Calcd for $C_{26}H_{34}N_4O_2Cl_4Pt\bullet 1/2CH_2Cl_2$: C, 39.1; H, 4.3; N, 6.8. Found: C, 38.9; H, 4.3; N, 6.5. The solvent of crystallization CH_2Cl_2 has been detected in the NMR spectra.

Conversion of *trans*-[$PtCl_2${N═C(CH_2CO_2Me)ON(Me)C(H)-(4-MeC_6H_4)}$_2$] 5a into the Corresponding Alkene 3a. (i) By the conventional method: a solution of **5a** (20.0 mg, 0.026 mmol) in dry CH_2Cl_2 (2.0 mL) was refluxed with stirring for 2 days to give the alkene **3a** (46% yield). (ii) By focused microwave irradiation in CH_2Cl_2: after 2 h at 80 °C, the alkene **3a** was isolated (51% yield).

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Supporting Information Available: Information concerning the material, instrumentation, and X-ray crystallographic data (and ORTEP drawings) for compounds **3a** and **5c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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