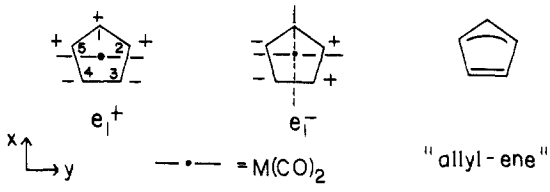
$(C_5Ph_5)M(CO)_2^-$. Crystal structures of $(C_5Me_5)Co(CO)_2$ and $(C_5Me_5)Rh(CO)_2$ show a significant departure of the rings from regular pentagons and reduction of molecular symmetry from pseudo-C_{2v} to C_s.[26,27] There are several reasons why this effect, if present in the radical anions, is unrelated to the ESR results. The plane of symmetry shown in the crystal structure is the xz-plane, bisecting the OC-M-CO angle. With this symmetry element, only d_{xy} can mix with d_{yz}. On MO theory grounds, it is difficult to see how such mixing could lead to lower energy. More significantly, however, d_{yz}-d_{xy} hybrids retain an axial dipolar hyperfine tensor, regardless of the degree of mixing, but the x- and z-axes are no longer principal axes of the resulting tensor. Since we are confident that the experimental g_x and A_x axes are coincident for $(1)^-$, this is good evidence against d_{yz}-d_{xy} mixing. From the most conservative viewpoint, there is reason to suspect Cp ring distortion to be less pronounced in the radical anions than in the neutral parents.

Lichtenberger et al.[27] argue that the loss of ring symmetry is due to the antibonding effect of the $2b_1(d_{xz})$ orbital. This effect may be visualized qualitatively in the following way. The highest energy ligand (Cp) orbitals taking part in the M-Cp bonding are the e_1^+ and e_1^- orbitals depicted below: In the e_1^+ orbital, which



interacts with M d_{xz} to form the HOMO in neutral $CpM(CO)_2$, the node is parallel to the OC-M-CO vector. The e_1^-, with a node perpendicular to the OC-M-CO vector, is of correct symmetry to interact with M d_{yz}, which is empty in the neutral 18-electron complex. To the extent that the e_1^-, d_{yz} interaction mixes into the ground state, electron withdrawal takes place from e_1^-, decreasing its contribution to the M-Cp bonding and leading to lengthening of the C_2-C_3 and C_4-C_5 bonds. This suggests the limiting "allyl-ene" structure shown, in which the "single" bonds average 1.447 Å.[27] It would be expected that partial population of the $2b_2(d_{yz})$ orbital in the 19-electron anion would attenuate this antibonding interaction, weakening the metal-Cp bonds, of course, but reducing the distortion of the ring.

Conclusions

1. The pentaphenylcyclopentadienyl ligand stabilizes the 19-electron anion radicals $(\eta^5\text{-}C_5Ph_5)M(CO)_2^-$ (M = Co, Rh) compared to their unsubstituted cyclopentadienyl analogues. As observed previously for isoelectronic Pd π-complexes, the thermodynamic stabilization ($E°$ potentials) is mild (a few hundred millivolts) but the kinetic stabilization is very high. The reduced Rh complex appears to be the best-characterized d^9 Rh(0) π-complex reported to date.

2. $(\eta^5\text{-}C_5Ph_5)Co(CO)_2^-$ shows no tendency to react with PPh_3, implying that the carbonyl ligands are strongly held in the 19-electron cobalt complex.

3. The 19-electron radical anions appear to have pseudo-C_{2v} symmetry, implying symmetrical bonding of the cyclopentadienyl ring to the metal. Half-occupation of the $2b_2(d_{yz})$ molecular orbital in the anion appears to relax the "allyl-ene" Cp distortion found in the neutral 18-electron complexes. McKinney and co-workers have shown[48] that the "allyl-ene" distortion is also absent in $[CpCo(PEt_3)_2]^+$. Thus, a relatively complete picture of the influence of electron count on metal-cyclopentadienyl bonding is now available for this class of compounds, with unsymmetrical metal-Cp interactions being found in the 18-electron complex but not in the 17- or 19-electron complexes.

4. There appears to be sufficient $(n+1)p_y$ admixture in the SOMO to significantly perturb the anisotropy of the g tensors for both the Co and Rh radical anions. While the effect of p_y admixture on the hyperfine tensor is probably small for the Co radical anion, it may be quite significant for the Rh species. Thus, our estimate of the 4d spin density for this species, $a^2 = 0.45$, is subject to considerable uncertainty.

Acknowledgment. We gratefully acknowledge support of this work by the National Science Foundation (CHE 83-03974), S.E.R.C. (Research Studentship to SJR), and N.A.T.O. We also thank the Johnson Matthey Co. for a loan of rhodium trichloride and J. Mevs. Dr. T. Gennett, and Dr. J. Edwin for experimental assistance.

Registry No. 1, 90502-88-8; 1^-, 103835-69-4; 2, 102539-06-0; 2^-, 103835-70-7.

(48) Harlow, R. L.; McKinney, R. J.; Whitney, J. F. *Organometallics* **1983**, 2, 1839.

$Pd(CH_3CN)_4(BF_4)_2$-Assisted Attack of Nitriles on Olefins. A Pd Analogue of the Ritter Reaction

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Abstract: The strongly electrophilic complex $Pd(CH_3CN)_4(BF_4)_2$ (1) activates a variety of olefins to undergo nucleophilic attack by nitriles to give nitrilium salts. These nitrilium salts undergo reaction with a variety of nucleophiles including electron-rich aromatics, alcohols, and amines, ultimately producing a variety of heterocyclic ring systems.

Palladium(II) salts are electrophilic and interact strongly with unsaturated electron-rich organic compounds. Thus, arenes, indoles, and other electron-rich heterocycles undergo direct palladation by palladium(II) acetate or trifluoroacetate.[1] In contrast, highly electrophilic $Pd(CH_3CN)_4(BF_4)_2$[2] (1) interacts strongly with olefins, with the proposed formation of incipient carbonium ions as intermediates, in its catalysis of the polymerization of ethylene and styrene,[3] its Friedel-Crafts alkylation of benzene with propene,[3] its rearrangements of *tert*-butylethylene and 1,1,2-trimethylcyclopropane to tetramethylethylene,[3] and its po-

(1) Fujiwara, Y.; Maruyama, O.; Yoshidomi, M.; Taniguchi, H. *J. Org. Chem.* **1981**, *46*, 851. Itahara, T.; Sakakibara, T. *Synthesis* **1978**, 607. Itahara, T. *Synthesis* **1979**, *151*; *J. Chem. Soc., Chem. Commun.* **1981**, 254. Itahara, T.; Ikeda, M.; Sakakibara, T. *J. Chem. Soc., Perkin Trans 1* **1983**, 1361.

(2) Schramm, R. F.; Wayland, B. B. *Chem. Commun.* **1968**, 898.

(3) Sen, A.; Lai, T.-W. *J. Am. Chem. Soc.* **1981**, *103*, 4627.

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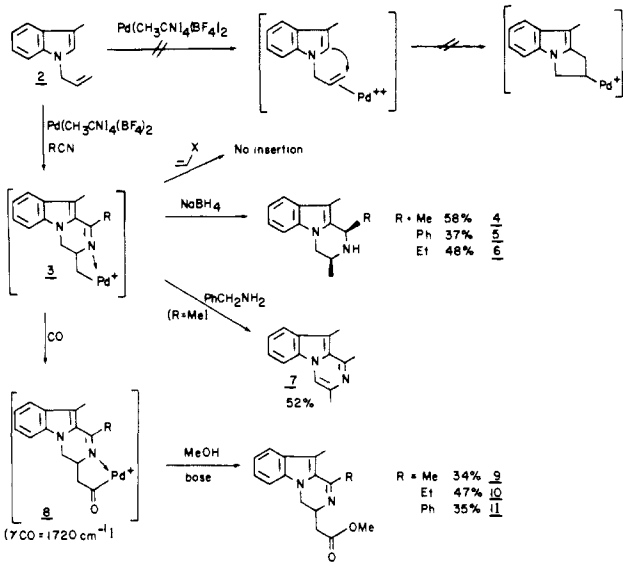
Scheme I



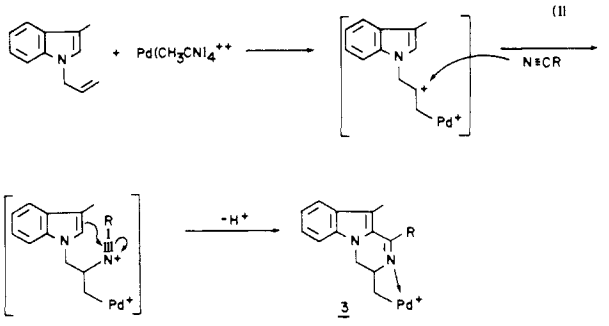
lymerization of acetylenes.[4] This complex also catalyzes the copolymerization of carbon monoxide with ethylene.[5] Related complexes, generated in situ by treatment of $PdCl_2$ with $AgBF_4$ in acetonitrile, efficiently cyclize the 2-position of 3-substituted indoles with remote olefin functionality to give polycyclic indole alkaloid ring systems.[6] We have recently reported an efficient palladium(0)-catalyzed route to N-allylindoloquinones.[7] Herein is described studies directed toward the cyclization of these species to pyrroloindoloquinones using $Pd(CH_3CN)_4(BF_4)_2$ (**1**) as the cyclizing reagent.

Results and Discussion

N-Allylskatole (**2**) was chosen as a model substrate with which to study the proposed cyclization. The results of the reaction of **2** with a stoichiometric amount of $Pd(CH_3CN)_4(BF_4)_2$ (**1**) under a variety of conditions are summaried in Scheme I. Under *no* conditions was the desired cyclization observed. When the reaction was carried out in nitromethane, mixtures of olefin dimerization products were obtained in low yield after reduction. In nitrile solvents a remarkable reaction occurred. A relatively stable (in solution) palladium complex, presumed to be **3**, was formed. Removal of solvent led to deposition of metallic palladium, preventing direct characterization of **3**. Reduction of **3** with sodium borohydride gave 1,2,3,4-tetrahydropyrazino[1,2-*a*]indoles **4–6** in fair yield. The stereochemistry was assigned as syn (containing a 1,3-pseudodiaxial proton configuration at the chiral C_1 and C_3 positions) by Nuclear Overhauser Enhancement (NOE) studies (see Experimental Section). When complex **3** was treated with triphenylphosphine prior to reduction, both syn and anti isomers were obtained (1:1.4 ratio). Thus, reduction of **3** probably occurred from the face opposite the Pd in the relatively rigid chelate system. Addition of phosphine would displace the chelated nitrogen, allowing rotation of the ring system and permitting reduction from both faces of the molecule.

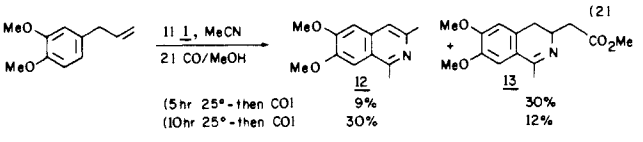
Treatment of **3** with an excess of benzylamine resulted in β-hydride elimination and rearrangement to give pyrazinoindole **7** in low yield. This material was relatively unstable and difficult to purify, hence the low yield. Although most σ-alkylpalladium(II) complexes undergo facile insertion reactions with a variety of olefins,[8] complex **3** did not react with either electron-poor (methyl acrylate) or electron-rich (*N*-vinylacetamide) olefins under a variety of conditions. Carbon monoxide, however, readily inserted to produce a new acylpalladium complex **8**, having an appropriate infrared absorption (γ_{CO} 1720 cm^{-1}) for a cationic σ-acylpalladium(II) complex.[9] This complex was stable in acetonitrile solution but decomposed upon solvent removal or precipitation. Cleavage of these complexes with methanol produced esters **9–11** in modest yield.

A reasonable mechanism for the formation of **2** is shown in eq 1. Palladation of the *N*-allyl group with the highly electrophilic **1** produces an intermediate having (at least) incipient carbonium ion character.[3] Attack of this cation by nitrile followed by

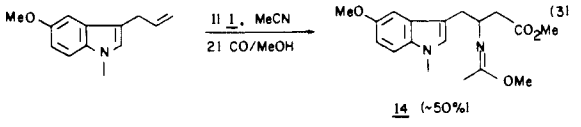


alkylation of the nitrilium salt by the nucleophilic 2-position of the indole[10] generates **3**, a σ-alkylpalladium(II) complex stabilized by chelation.[11] This process bears a striking resemblance to the classic Ritter reaction,[12] with the fundamental difference that Pd^{2+} is used in place of a strong acid, and remains in the ultimate condensation product, permitting the subsequent introduction of further functionality.

Electron-rich allylbenzene derivatives such as methyleugenol have been converted to isoquinoline derivatives via the Ritter reaction.[12c] Similarly, **1** effected this cyclization (eq 2). In this



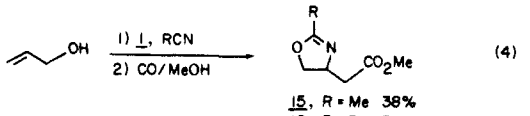
case, the intermediate σ-alkylpalladium species underwent slow, spontaneous β-hydride elimination and olefin migration to produce the isoquinoline derivatives **12**, as well as carbon monoxide insertion to produce the dihydroisoquinoline ester **13**. Allylbenzene itself did not condense with acetonitrile under these conditions but was converted to phenylacetone and its dimethyl ketal by Wacker-type chemistry (nucleophilic attack of methanol on the Pd-complexed olefin).[13] 1-Methyl-3-allyl-5-methoxyindole gave yet a different type of product, imidate **14**, from attack of the nitrile on the olefin and subsequent reaction of the nitrilium salt with methanol rather than with the electron-rich aromatic system (eq 3).



These examples indicate that the ultimate fate of the nitrilium ion is strongly dependent on the nature of the nucleophilic species

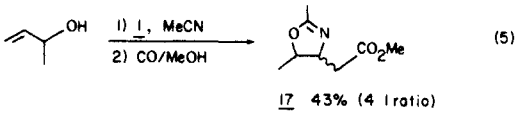
(4) Sen, A.; Lai, T.-W. *Organometallics* **1982**, *1*, 415.
(5) Lai, T.-W.; Sen, A. *Organometallics* **1984**, *3*, 866.
(6) Trost, B. M.; Godleski, S. A.; Genet, J. P. *J. Am. Chem. Soc.* **1978**, *100*, 3930. Trost, B. M.; Godleski, S. A.; Belletire, J. L. *J. Org. Chem.* **1979**, *44*, 2052. Trost, B. M.; Fortunak, J. M. D. *Organometallics* **1982**, *1*, 7.
(7) Hegedus, L. S.; Mulhern, T. A.; Mori, A. *J. Org. Chem.* **1985**, *50*, 4282.
(8) Collman, J. P.; Hegedus, L. S. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1980; pp 580–585.
(9) Hegedus, L. S.; Hansen, K.-S. *J. Am. Chem. Soc.* **1975**, *97*, 1184. Hegedus, L. S.; Anderson, O. P.; Zetterberg, K.; Allen, G.; Hansen, K.-S.; Olsen, D. J.; Packard, A. B. *Inorg. Chem.* **1977**, *16*, 1887.
(10) Remers, W. A. In *Indoles*; Houlihan, W. J., Ed.; Wiley: New York, 1972; Part 1, pp 1–226.
(11) Reference 8, pp 592–597.
(12) (a) Ritter, J. J.; Minari, J. K. *J. Am. Chem. Soc.* **1948**, *70*, 4045. (b) Meyers, A. I.; Sircar, J. C. In *The Chemistry of the Cyano Group*; Rappoport, Z., Ed.; Wiley Interscience: New York, 1970; pp 358–380. (c) Krimen, L. I.; Cota, D. J. *Org. React.* **1969**, *17*, 213.
(13) Tsuji, J. *Organic Synthesis with Palladium Compounds*; Springer-Verlag: Berlin, 1980; pp 13–16.

present, and nucleophiles other than electron-rich arenes may preferentially attack. Indeed, with unsaturated alcohols as substrates intramolecular trapping of the nitrilium ion by alkoxide was observed (eq 4–6). Again, the process was very sensitive to



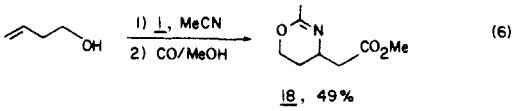
(4)

15, R = Me 38%
16, R = Ph 30%



(5)

17 43% (4 I ratio)

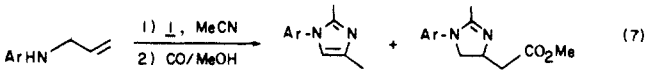


(6)

18, 49%

the structure of the substrate. Methallyl alcohol, cinnamyl alcohol, and cyclohexen-3-ol led to intractable mixtures of products, and *o*-allylphenol produced 2-methylbenzofuran[14] under the same conditions.

N-Allylanilines are electron-rich aromatic compounds which potentially may react with the intermediate nitrilium species either at nitrogen or on the aromatic ring. However, only the former mode was observed even with very electron-rich systems (eq 7).



(7)

19, Ar=Ph 26-51% 20, 19-40%
21, Ar=2,5-diMeOPh 22% 22, 24%

When attack by nitrogen was prevented by N-alkylation (e.g., *N*-methyl-*N*-allylaniline), no nitrile incorporation was observed. Rather a mixture of starting material (10%), *N*-methylaniline (38%—from deallylation of the amine), and *N*-acetonylaniline (11%—from Wacker oxidation of the allyl group) was obtained.

Thus, $Pd(CH_3CN)_4(BF_4)_2$ activates olefins to undergo attack by (solvent) nitriles to generate unstable nitrilium salts. These undergo intramoleuclar attack by some electron-rich arenes, and either intermolecular or intramolecular attack by alcohols and amines to generate relatively stable σ-alkylpalladium(II) complexes (e.g., eq 1), which undergo facile CO insertion and/or β-hydride elimination reactions.

Experimental Section

General. Melting points were taken with a Mel-Temp apparatus and are uncorrected. Infrared spectra were recorded on a Beckman 4240 spectrometer. ^1H NMR spectra were recorded with a Varian T-60 (60 MHz), and IBM-Bruker WP270SY (270 MHz), or a Nicolet NTCFT 1180 (360 MHz) spectrometer with tetramethylsilane (Me_4Si) as an internal standard. Routine mass spectra were taken on Vacuum Generators MM16 spectrometer with a Systems Industries interface and disk drive with a Digital PDP8A computer at 70 eV. Liquid chromatography was carried out under moderate pressures (20–60 psi) either by using columns of appropriate size packed with Merck silica gel 60 (40–60 mesh) or by using a Chromatotron (Harrison Research) radial-layer chromatographic device with plates of Kieselgel 60 PF 254 silica gel. Unless otherwise stated all reactions were run under an argon atmosphere. Elemental analyses were performed by M-H-W Laboratories, Phoenix, AZ.

Materials. Acetonitrile was distilled over CaH_2 after treatment with silica gel and was stored under argon with molecular sieves. Methanol was distilled over Mg–I_2 after heating at reflux and was stored with anhydrous $CaSO_4$. All substrates and solvents were distilled prior to use. $Pd(CH_3CN)_4(BF_4)_2$ (**1**) was prepared by literature methods.[2,5]

General Method for Palladium(II)-Mediated Addition of Nitriles to Olefins. A flame-dried 50-mL two-necked flask fitted with a magnetic stirring bar, a rubber serum cap, and a vacuum adapter was charged with $Pd(MeCN)_4(BF_4)_2$ (**1**) (0.22 g, 0.50 mmol) and placed under an argon atmosphere. The dry degassed nitrile (2 mL) was added to the Pd^{2+} salt via syringe, and the mixture was stirred for 2–3 min at room temperature. A solution of the olefin (0.50 mmol) dissolved in 8–10 mL of the nitrile was added to the Pd^{2+} complex via syringe using a syringe pump to control the rate of addition. Depending on the substrate, the addition time was varied from 2 to 20 h. The resulting complex was then treated in one of several ways.

Method A. The flask was cooled in an ice bath, and 5 mL absolute ethanol was added via syringe. After 5 min, $NaBH_4$ (0.5–2.0 mmol) was slowly added as a solid and the resulting mixture stirred under positive argon pressure for 1 h. Saturated aqueous NH_4Cl was then added to quench the reaction, and the mixture was stirred for an additional 5 min. The resulting black suspension was filtered through Celite to remove Pd(0). The Celite was washed with ether, and the filtrate was transferred to a separatory funnel. The phases were separated and the aqueous phase was extracted with ether (3X). The combined organic phase was washed with 5% aqueous HCl (3X). The combined acidic phase was made basic (pH ~10) with 2 N NaOH and extracted with ether (3X). The resulting ether phase was washed with brine (1X) and dried ($MgSO_4$). Filtration followed by concentration of the filtrate in vacuo afforded the purified product as the free base.

Method B. The flask was evacuated and then filled with carbon monoxide from a rubber balloon. The mixture was stirred vigorously at room temperature for 3 h. Methanol (5 mL) was then added via syringe, and the resulting mixture was allowed to stir at room temperature for 12–24 h. The resulting black suspension was filtered through Celite to remove Pd(0). The Celite was washed with fresh methanol, and the filtrate was concentrated in vacuo to afford the crude ester as its HBF_4 salt. Alternatively, the acid salt slurried in 5 mL of methanol was shaken with saturated $NaHCO_3$ in a separatory funnel. The basic mixture was extracted with ether (3X). The combined ether layer was washed with brine (1X), dried ($MgSO_4$), and suction filtered. The filtrate was concentrated in vacuo to afford the crude methyl ester as a free base.

Preparation of *cis*-1,2,3,4-Tetrahydro-1,3,1-trimethylpyrazino[1,2-*a*]indole (4). A solution of *N*-allylskatole (**2**)[15] (0.10 g, 0.58 mmol) in 10 mL of CH_3CN was added to complex **1** (0.25 g, 0.57 mmol) in 2 mL of CH_3CN over the course of 10 h as described in the General section. After stirring an additional 3 **h**, the mixture was diluted with 5 mL of EtOH, reduced with $NaBH_4$ (0.04 g, 1.1 mmol), and isolated as described in the General section, method A, to give **4** (0.071 g, 58%) as an air-sensitive bright-yellow oil suitably pure for further use. An analytical sample was obtained as the HCl salt, recrystallized from EtOH to give a gold powder: mp 258 °C (d); IR (KBr) 3400, 2920, 2830, 2770, 2460, 2320, 1570, 1540, 1452, 1371, 1346, 1322, 1295, 1230, 1210, 1196, 1140, 1095, 1005, 750 cm^{-1}. Anal. ($C_{14}H_{19}N_2Cl$) C, H, N.

Free Base 4. Peak assignments were made with the aid of homonuclear decoupling: ^1H NMR (360 MHz, $CDCl_3$) δ 1.34 (d, J = 6.3 Hz, 3, C_3–CH_3), 1.63 (d, J = 6.5 Hz, 3, C_1–CH_3), 2.33 (s, 3, C_{10}–CH_3), 3.25 (m, 1, $NCH_2CH(Me)NHCH(Me)$), 3.51 (t, J = 11.2 Hz, 1, $NCH_aH_bCH(Me)NHCH(Me)$), 4.13 (dd, J = 3.7, 11.2 Hz, 1, $NCH_aH_bCH(Me)NHCH(Me)$), 4.40 (q, J = 6.5 Hz, 1, $NCH_2CH(Me)NHCH(Me)$), 7.08–7.35 (m, 3, aromatic), 7.52 (d, J = 7.7 Hz, 1, C_9–H); IR (CCl_4) 3300 (NH), 3050, 2960, 2920, 2860, 1596, 1540, 1458, 1380, 1366, 1325, 1310, 1295, 1245, 1220, 1198, 1150, 1120, 1005 cm^{-1}; mass spectrum, m/e (relative intensity) 214 (29, parent), 213 (17, $P^+ - H$), 212 (68, $P^+ - 2H$), 100 (100, $P^+ - H - Me$), 197 (63, $P^+ - 2H - Me$), 170 (30, $P^+ - C_2H_6N$).

***trans*-1,2,3,4-Tetrahydro-1,3,10-trimethylpyrazino[1,2-*a*]indole (4′).** A solution of indole **2** (0.11 g, 0.63 mmol) in 10 mL of CH_3CN was added to complex **1** (0.28 g, 0.63 mmol) in 2 mL of CH_3CN over the course of 2.5 h as described in the General section. The mixture was stirred for a total of 18 h at room temperature. A solution of triphenylphosphine (0.17 g, 0.63 mmol) in 4 mL of CH_3CN was then added via syringe, and the mixture was stirred an additional 10 min. The resulting mixture was cooled in an ice bath, diluted with 5 mL EtOH, and treated with $NaBH_4$ (0.05 g, 1.24 mmol) as described in the General section (method A). Product isolation in the usual way afforded **4′** (0.08 g, 58%) as an air-sensitive mixture of diastereoisomers which was used for NOE experiments without further purification. The NMR spectral data showed that the mixture consisted of *trans*- and *cis*-**4** in a ratio of 1.4:1 (ca. 17% de). Attempted separation (SiO_2: hexanes–ethyl acetate mixtures) was unsuccessful. Due to the air-sensitive nature of these products, no further efforts were made to effect separation. NMR

(14) Hosokawa, T.; Yamashita, S.; Murahashi, S.; Sonoda, A. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 3662.

(15) Kikugawa, Y.; Miyake, Y. *Synthesis* **1981**, *461*.

Table I.

irradiate	observe	NOE % cis[a]	NOE % trans[b]
C_1–H	C_3–H	6.0	0.0
C_3–H	C_1–H	6.9	0.0
C_1–Me	C_3–H	0.0	5.9
C_3–Me	C_1–H	0.0	0.0

[a] Obtained from a pure sample of *cis*-**4**. [b] Obtained from a 1.4:1[c] mixture of trans:cis. [c] Determined by NMR.

spectral data for *trans*-**4** were obtained from this mixture of diastereoisomers. Peak assignments were made with the aid of homonuclear decoupling and by comparison of coupling constants and chemical shifts obtained from the mixture with those obtained from pure *cis*-**4**.

Compound **4**: ^{1}H NMR (360 MHz, $CDCl_3$) δ (d, J = 6.3 Hz, 3, C_3CH_3), 1.46 (d, J = 7.0 Hz, 3, C_1–CH_3), 2.21 (s, 3, C_{10}–CH_3), 3.25 (t, J = 10.9 Hz, 1, NCH_aH$_b$CH(Me)NHCH(Me)), 4.08 (m, 1, NCH$_a$$H_b$CH(Me)NHCH(Me)), 4.47 (q, J = 7.0 Hz, NCH$_2$CH(Me)-NHCH(Me)), 7.00–7.20 (m, 3, aromatic), 7.44 (m, 1, C_9–H).

The results of the NOE measurements are shown in Table I.

1,2,3,4-Tetrahydro-1-phenyl-3,10-dimethylpyrazino[1,2-*a*]indole (5). The reaction was run as above, except benzonitrile was used as solvent rather than acetonitrile. Thus, when 0.12 g (0.70 mmol) of **2** was used, 0.31 g (0.70 mmol) of **1** in 6 mL of benzonitrile with addition over 11.5 h gave 0.07 g (37%) of **5**: ^{1}H NMR (360 MHz, $CDCl_3$) δ 1.34 (d, J = 6.3 Hz, 3, C_3–CH_3), 1.63 (s, 3, C_{10}–CH_3); AMX pattern, δ_A 3.43, δ_M 3.66, δ_X 4.22 (3, J_{AX} = 3.6, J_{AM} = 10.8, J_{MX} = 10.9 Hz, CH_2CHN), 7.2–8.0 (m, 10, ArH); mass spectrum, m/e 276 (parent). This material was never completely separated from benzylamine (from reduction of benzonitrile). Hence, acceptable analytical data were not obtained, and its structure was inferred from NMR and mass spectra, and by analogy with **11**, which was fully characterized.

3,10-Dimethyl-1-ethyl-1,2,3,4-tetrahydropyrazino[1,2-*a*]indole (6). A solution of indole **2** (0.09 g, 0.53 mmol) in 8 mL of propionitrile was added to complex **1** (0.22 g, 0.51 mmol) in 2 mL of propionitrile over the course of 2.75 h as described in the General section. After a total reaction time of 8.3 h, the resulting complex was diluted with 5 mL of EtOH, reduced with $NaBH_4$ (0.04 g, 1.0 mmol), and isolated as described in method A to give **6** (0.056 g, 48%) as a bright-yellow air-sensitive oil suitably pure for further use. For elemental analysis, **6** was converted to its HCl salt. The crude salt was recrystallized from ethanol to give an analytical sample as a mustard-yellow solid: mp 233 °C dec; IR (KBr) 3400, 2910, 2870, 2800–2700, 2355, 2330, 1596, 1541, 1521, 1460, 1340, 1330, 1309, 1239 cm^{-1}. Anal. ($C_{15}H_{21}N_2Cl$) C, H, N.

Free Base: ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.97 (t, J = 7.6 Hz, 3, ArCHCH$_2$CH_3), 1.30 (d, J = 6.3 Hz, 3, NCH$_2$CH(CH_3)NH), 1.96 (m, 1, ArCHCH_aH$_b$CH$_3$), 2.10 (m, 1, ArCHCH$_a$$H_bCH_3$), 2.29 (s, 3, C_{10}–CH_3), 3.12 (m, 1, NCH$_2$CH(CH$_3$)NH), 3.48 (t, J = 11.0, 1, NCH_aH$_b$CH(CH$_3$)NH), 4.10 (dd, J = 3.4, J = 11.0 Hz, NCH$_a$$H_b$CH-(CH$_3$)NH), 4.34 (m, 1, ArCHC$H_2CH_3$), 7.09–7.23 (m, 3, aromatic), 7.52 (m, 1, C_9–H); IR ($CDCl_3$) 3300, 3055, 2965, 2925, 2870, 1593, 1470, 1460, 1419, 1381, 1370, 1359, 1324, 1308, 1238, 1216, 1194, 1150, 1120, 1098, 1050, 1010 cm^{-1}; mass spectrum, m/e (relative intensity) 228 (11, parent), 227 (18, P$^+$ – H), 226 (94, P$^+$ – 2H), 211 (71, P$^+$ – 2H – Me), 199 (100, P$^+$ – Et).

1,3,10-Trimethylpyrazino[1,2-*a*]indole (7). A solution of **2** (0.14 g, 0.81 mmol) in 9 mL of CH_3CN was added to a solution of **1** (0.33 g, 0.75 mmol) in 3 mL of CH_3CN over the course of 2.5 h as described in the General section. The mixture was stirred at room temperature for a total of 20 h, and benzylamine (0.82 mL, 7.5 mmol) was then added via syringe. The mixture was stirred at room temperature for 168 h and was then chromatographed on a short column of neutral alumina (approximately 2 g), eluting with ethyl acetate. The eluent was concentrated in vacuo to give an amber oil (0.810 g). Purification by liquid chromatography (neutral Al_2O_3; 3:1, hexanes:ethyl acetate, gradient) gave **7** (0.083 g, 52%) as a yellow solid: mp 99–100 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.40 (d, J = 0.7 Hz, C_{10}–CH_3), 2.76 (s, 3, C_1–CH_3 or C_3–CH_3), 2.86 (s, 3, C_3–CH_3 or C_1–CH_3), 7.35 (m, 2 or 3, aromatic), 7.77 (m, 3 or 2, aromatic); IR (KBr) 3040, 2960, 2915, 1850, 1617, 1603, 1455, 1428, 1394, 1372, 1330, 1309, 1286, 1236, 1190, 1160, 1113, 1016, 970, 945, 800, 731, 710, 683 cm^{-1}; mass spectrum, m/e (relative intensity) 210 (75, parent), 209 (100, P$^+$ – H). Anal. ($C_{14}H_{14}N_2$) C, H, N.

3-(Carbomethoxymethyl)-3,4-dihydro-1,10-dimethylpyrazino[1,2-*a*]-indole (9). A solution of indole **2** (0.11 g, 0.64 mmol) in 8 mL of CH_3CN was added to a solution of complex **1** (0.27 g, 0.61 mmol) in 2 mL of CH_3CN over the course of 2.5 h as described in the General section. After a total of 5.3 h, the mixture was placed under a CO atmosphere (2 h) and treated with 5 mL of MeOH (14 h), and the crude product was isolated as described in method B. Purification by liquid chromatography (neutral Al_2O_3; 3:1, hexanes:ethyl acetate) gave **7** (0.01 g, 7%, R_f 0.52) as a yellow oil and **9** (0.06 g, 34%, R_f 0.16) as pale-yellow needles: mp 116–117 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.50 (d, J = 1.4 Hz, 3, C_1–CH_3 or C_{10}–CH_3), 2.54 (s, 3, C_{10}–CH_3 or C_1–CH_3), 2.60 (dd, J = 8.4, 16.0 Hz, 1, NCH$_2$CHCH_aH$_b$CO$_2$Me), 2.91 (dd, J = 5.5, 16.0 Hz, 1, NCH$_2$CHCH$_a$$H_bCO_2$Me), 3.68 (m, 1, NC$H_aH_b$CHCH$_2CO_2$Me), 3.73 (s, 3, OCH$_3$), 4.25 (m, 2, NCH$_a$$H_b$CHCH$_2CO_2$Me), 7.11 (m, 1, aromatic), 7.28 (m, 2, aromatic), 7.62 (d, J = 7.9 Hz, 1, C_9–H); IR (KBr) 3055, 3025, 2985, 2910, 2860, 1730 (C=O), 1593, 1530, 1488, 1467, 1439, 1418, 1390, 1352, 1341, 1321, 1280, 1251, 1238, 1228, 1186, 1170, 1125, 1105, 1072 cm^{-1}. Anal. ($C_{16}H_{18}N_2O_2$) C, H, N.

Spectral Data for Intermediate Acylpalladium Complex 8: IR (CH_3-CN) 3150, 2975, 2925, 2275 (CN), 2235 (CN), 1950 (Pd–CO), 1720 (CH$_2$C(O)Pd), 1600, 1540, 1360, 1090 (BF_4), 1024 (BF_4) cm^{-1}.

3-(Carbomethoxymethyl)-3,4-dihydro-1-ethyl-10-methylpyrazino[1,2-*a*]indole (10). A solution of indole **2** (0.13 g, 0.75 mmol) in 8 mL of CH_3CN was added to **1** (0.32 g, 0.72 mmol) in 2 mL of CH_3CN over the course of 2.5 h as described in the General section. The mixture was stirred at room temperature for a total of 10 h and then placed under a CO atmosphere (2.5 h) and treated with 5 mL of MeOH (8.5 h) and the crude product isolated as described in method B. Purification by liquid chromatography (neutral Al_2O_3; 5:1–3:1, hexanes:ethyl acetate, gradient), collecting the band at R_f 0.22 (Al_2O_3 type E: 5:1, hexanes:ethyl acetate), gave **10** (0.096 g, 47%) as an off-white flaky solid: mp 69.5–70 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.24 (t, J = 7.5 Hz, 3, CH$_2$CH_3) 2.54 (s, 3, C_{10}–CH_3), 2.58 (m, 1, NCH$_2$CHCH_aH$_b$CO$_2$Me), 2.81 (m, 3, NCH$_2$CHCH$_a$$H_bCO_2$Me and C$H_2CH_3$), 3.70 (m, 1, NC$H_aH_b$CHCH$_2CO_2$Me), 3.71 (s, 3, OCH$_3$), 4.22 (m, 2, NCH$_a$$H_b$CHCH$_2CO_2$Me), 7.13 (m, 1, aromatic), 7.26 (m, 2, aromatic), 7.62 (d, J = 7.9 Hz, 1, C_9–H); IR (KBr) 3045, 2965, 2950, 2905, 2895, 2860, 1734 (C=O), 1599, 1468, 1447, 1432, 1418, 1386, 1354, 1322, 1316, 1268, 1220, 1181, 1165, 985, 725 cm^{-1}. Anal. ($C_{17}H_{20}N_2O_2$) C, H, N.

3-(Carbomethoxymethyl)-3,4-dihydro-10-methyl-1-phenylpyrazino-[1,2-*a*]indole (11). A solution of indole **2** (0.13 g, 0.75 mmol) in 8 mL of benzonitrile was added to a solution of complex **1** (0.32 g, 0.71 mmol) over the course of 3 h as described in the General section. After stirring at room temperature for an additional 11 h, the mixture as placed under a CO atmosphere (1 h), treated with 5 mL of methanol, and stirred for 12 h as described in method B. Product isolation as in method B followed by removal of excess benzonitrile by evaporative distillation gave the crude free base **11**. Liquid chromatography (neutral Al_2O_3, type E: 7:1–1:1, hexanes:ethyl acetate, gradient) followed by precipitation from hexanes afforded **11** (0.082 g, 35%) as a pale-yellow powder: mp 110–111 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.95 (s, 3, C_{10}–CH_3), 2.64 (dd, J = 8.5, 16.0 Hz, 1, NCH$_2$CHCH_aH$_b$CO$_2$Me), 3.03 (dd, J = 5.0, 16.0 Hz, 1, NCH$_2$CHCH$_a$$H_bCO_2$Me), 3.73 (s, 3, OCH$_3$), 3.84 (m, 1, NC$H_aH_b$CHCH$_2CO_2$Me), 4.26 (m, 2, NCH$_a$$H_b$CHCH$_2CO_2$Me), 7.12 (m, 1, aromatic), 7.33 (m, 2, aromatic), 7.44 (m, 3, aromatic), 7.59 (m, 3, aromatic); IR (KBr) 3055, 3025, 2985, 2965, 2945, 2915, 2890, 2860, 1736 (C=O), 1585, 1564, 1468, 1431, 1419, 1389, 1370, 1343, 1327, 1317, 1300, 1290, 1260, 1240, 1228, 1161, 1000, 990, 770, 738, 722, 695 cm^{-1}. Anal. ($C_{21}H_{20}N_2O_2$) C, H, N.

6,7-Dimethoxy-1,3-dimethylisoquinoline (12). A solution of methyleugenol[16] (0.11 g, 0.63 mmol) in 15 mL of CH_3CN was added to complex **1** (0.28 g, 0.63 mmol) in 2 mL of CH_3CN over the course of 10 h in the previously described way. After a total of 35.5 h the mixture was cooled in an ice bath, diluted with 5 mL of EtOH, and subsequently reduced with $NaBH_4$ (0.024 g, 0.63 mmol) for 0.75 h. The mixture was diluted with Et_2O and stirred for 2.5 h at room temperature. The resulting black suspension was filtered through Celite. The Celite was washed with additional ether, and the filtrate was subjected to the acid–base extraction and isolation sequence described in method A. Recrystallization from ether/hexanes gave **12** (0.043 g, 31%) as a white solid: mp 120–121 °C [lit.[17] mp 121.5 °C]; ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.61 (s, 3, Ar–CH_3), 2.87 (s, 3, Ar–CH_3), 4.00 (s, 3, OCH$_3$), 4.02 (s, 3, OCH$_3$), 6.96 (s, 1, aromatic), 7.22 (s, 1, aromatic), 7.23 (s, 1, aromatic).

Reaction of Methyleugenol with 1 Followed by CO To Give 13. Complex **1** (133.2 mg, 0.30 mmol) in CH_3CN (2 mL) and methyleugenol (59 mg, 0.33 mmol) in CH_3CN (8 mL) were stirred at room temperature under Ar for 10 h and then with MeOH (3 mL) under CO for 18 h as shown in the General procedure. The normal isolation of the resulting mixture gave a yellow oil, which was purified by an alumina column (hexane:EtOAc = 4:1 ~ 2:1 ~ EtOAc) to yield 6,7-dimethoxy-1,3-di-

(16) Johnstone, R. A. W.; Rose, M. E. *Tetrahedron* **1979**, *35*, 2169.
(17) Bruckner, V.; Kardos, V. *Ann.* **1935**, *518*, 226.

methylisoquinoline (**12**) (20 mg, 30%) as a white solid and 3,4-dihydro-6,7-dimethoxy-3-[(methoxycarbonyl)methyl]-1-methylisoquinoline (**13**) (10 mg, 12%) as a yellow oil.

Compound 13: ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.37 (d, 3, 1-Me, J = 1.6 Hz), 2.45–2.65 (m, 2, CH_2 in the ring), 2.78 (dd, 1, one of CH_2COOMe, J_1 = 15.6, J_2 = 5.3 Hz), 2.89 (dd, 1, one of CH_2COOMe, J_1 = 15.6, J_2 = 5.9 Hz), 3.72 (s, 3, $COOCH_3$), 3.88 (m, 1, CH–N), 3.91 (s, 6, 6,7-CH_3O), 6.69 (s, 1), 6.99 (s, 1); IR ($CDCl_3$) 2950, 1733 (C=O), 1625, 1603, 1570, 1505 cm^{-1}. Anal. ($C_{13}H_{15}NO_2$) C, H, N.

Similarly, **1** (400 mg, 0.90 mmol) in CH_3CN (10 mL) and methyleugenol (174 mg, 0.97 mmol) in CH_3CN (10 mL) were stirred at room temperature under Ar for 5 h and then with MeOH under CO for 16 h. The normal isolation of the resulting mixture gave a brown oil (197 mg), which was then separated by an alumina column (hexane:EtOAc = 4:1 ~ 1:1 ~ EtOAc) to yield **12** (18 mg, 9%) as a white solid and **13** (74 mg, 30%) as a yellow oil.

Reaction of 3-Allyl-5-methoxy-1-methylindole[15] with 1. Complex **11** (133.2 mg, 0.30 mmol) and the indole (65 mg, 0.32 mmol) were stirred under Ar for 6 h and with MeOH (3 mL) under CO for 16 h. Isolation gave a dark-brown oil, which was purified by the column chromatography (alumina, hexane:ethyl acetate = 4:1 ~ 1:1) to give 57 mg (~50%) of a yellow oil, which hydrolyzed readily: ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.64 (s, 3, CH_3C=N), 2.58 (m, 2, CH_2CH—CH_2COOMe), 2.7–3.0 (2 sets of dd, 2, CH_2COOMe), 3.58 (s, 3, CH_3OC=N or $COOCH_3$), 3.61 (s, 3, CH_3OC=N or $COOCH_3$), 3.71 (s, 3, N—CH_3), 3.86 (s, 3, OCH_3), 4.00 (m, 1, CH—N), 6.79 (s, 1, 2-H), 6.86 (m, 1, 6-H), 7.14 (d, 1, 4-H), 7.16 (d, 1, 7-H, J = 8.8 Hz); IR ($CDCl_3$) 2950, 1740 (C=O), 1685 (C=N), 1495; mass spectrum (chemical ionization) $M^+ + 1$ = 333. This material decomposed on standing and was not further characterized.

General Reaction Procedure for Allyl Alcohols and Allylamines. To $Pd(CH_3CN)_4(BF_4)_2$ (133.2 mg, 0.30 mmol) placed under Ar atmosphere was added dry degassed acetonitrile (2 mL), and the mixture was stirred for a few minutes. Then olefin (0.31~0.33 mmol) in the dry degassed acetonitrile (8 mL) was added to the stirred slightly yellow **1** in acetonitrile over 2 h by using a syringe pump. The mixture was stirred for a proper period at 25 °C. The reaction system was then evacuated, and CO gas was introduced with a balloon followed by the addition of dried methanol (3 mL). The resulting mixture was stirred for 16–18 h at 25 °C and then filtered through Celite to separate palladium black. The filtrate was washed with aqueous $NaHCO_3$, extracted with ether, washed with brine, dried over $MgSO_4$, filtered, and concentrated in vacuo to give a crude product, which was then purified.

Reaction of Allyl Alcohol with Acetonitrile To Form 15. The mixture of **1** in CH_3CN (2 mL) and allyl alcohol (18 mg, 0.31 mmol) in CH_3CN (8 mL) was stirred at 25 °C under Ar for a total of 5.5 h and then under CO for 2.5 h and with MeOH (3 mL) under CO for 16 h. Filtration through Celite gave a colorless solution, which was then isolated in the general way to give a brownish yellow oil. This oil was bulb-to-bulb distilled in vacuo (0.025 mmHg) to give 18 mg (38%) of 4-[(methoxycarbonyl)methyl]-2-methyl-2-oxazoline (**15**) as a colorless oil: ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.98 (s, 3, OCH_3), 2.44 (dd, 1, one of CH_2COOCH_3, J_1 = 16.3, J_2 = 8.4 Hz), 2.79 (dd, 1, one of CH_2COOCH_3, J_1 = 16.3, J_2 = 5.1 Hz), 3.70 (s, 3, OCH_3), 3.93 (m, 1, N—CH), 4.43 (m, 2, OCH_2—CH); IR ($CDCl_3$) 2955, 1737 (C=O), 1675 (C=N), 1440, 1390, 1236 cm^{-1}. Anal. ($C_7H_{11}NO_3$) C, H, N.

Reaction of Allyl Alcohol with Benzonitrile To Form 16. The mixture of **1** (133.2 mg, 0.30 mmol) in benzonitrile (2 mL) and allyl alcohol (18 mg, 0.31 mmol) in benzonitrile (3 mL) was stirred at 25 °C under Ar for 6 h and then with MeOH (3 mL) under CO for 18 h. The resulting mixture was filtered through Celite to give a slightly yellow solution. The normal isolation gave a colorless benzonitrile solution, which was purified by column chromatography (alumina, 20 mm × 20 cm, hexane (for benzonitrile) and then EtOAc/MeOH) to give **16** as a colorless oil (21 mg, 30%): ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.50 (dd, 1, one of CH_2COOMe, J_1 = 16.5, J_2 = 9.0 Hz), 2.94 (dd, 1, one of CH_2COOMe, J_1 = 16.5, J_2 = 4.7 Hz), 3.70 (s, 3, OCH_3), 4.12 (m, 1, N—CH), 4.60–4.64 (m, 2, OCH_2), 7.35–7.45 (m, 3), 7.91 (m, 2); IR ($CDCl_3$) 2955, 1738 (C=O), 1648 (C=N), 1438, 1168 cm^{-1}. Anal. ($C_{12}H_{13}NO_3$) C, H, N.

Reaction of 1-Buten-3-ol with Acetonitrile To Give 17. The mixture of **1** (133.2 mg, 0.30 mmol), in CH_3CN (2 mL) and substrate (25 mg, 0.34 mmol) was stirred at room temperature under Ar for 5.5 h and then under CO for 3.5 h and with MeOH (3 mL) under CO for 16 h. Filtration through Celite gave a colorless solution, which was then worked up in the general way to give a slightly yellow liquid. This crude liquid, almost pure by ^{1}H NMR, was bulb-to-bulb distilled in vacuo (0.025 mmHg) to give 22 mg (43%) of 4-[(methoxycarbonyl)methyl]-2,5-dimethyl-2-oxazoline (**17**) as a colorless liquid in the dry ice trap: ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.36 (d, 3, $CHCH_3$, J = 6.2 Hz), 1.96 (s, 3, CH_3C=N), 2.40 (dd, 1, one of CH_2COOCH_3, J_1 = 16.1, J_2 = 8.7 Hz), 2.70 (dd, 1, one of CH_2COOCH_3, J_1 = 16.1, J_2 = 5.5 Hz), 3.70 (s, 3, OCH_3), 3.95 (m, 1, N—CH), 4.30 (p, 1, CH_3CHO, J = 6.2 Hz) (The above NMR is of the major isomer; ratio of major/minor = 4); NMR is of minor isomer: 1.20 (s, $CHCH_3$, J = 6.4 Hz), 2.48 (dd, CH_2COOCH_3, J = 8.3 Hz), 2.63 (dd, CH_2COOCH_3, J = 6.7 Hz), 4.45 (m, CH—N), 4.80 (m, OCH—CH_3); IR ($CDCl_3$) 2950, 1735, (C=O), 1662 (C=N), 1436, 1231 cm^{-1}. Anal. ($C_8H_{13}NO_3$) C, H, N.

Reaction of 1-Buten-4-ol with Acetonitrile To Give 18. The mixture of **1** (133.2 mg, 0.30 mmol) in CH_3CN (2 mL) and the alcohol (23 mg, 0.31 mmol) in CH_3CN (8 mL) was stirred at 25 °C under Ar for 9 h and then with MeOH under CO for 19 h. Filtration of the resulting mixture gave a colorless solution, which was isolated as usual to give a yellow oil. This oil was bulb-to-bulb distilled in vacuo (0.025 mmHg) to give **18** (25 mg, 49%) as a colorless liquid: ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.4–1.7 (m, 2, OCH_2CH_2CH), 1.88 (s, 3, CH_3C=N), 1.95–2.05 (m, 1, NCH), 2.34 (dd, 1, one of CH_2COOCH_3, J_1 = 15.5, J_2 = 8.5 Hz), 2.66 (dd, 1, one of CH_2COOCH_3, J_1 = 15.5, J_2 = 6.3 Hz), 3.70 (s, 3, OCH_3), 4.05–4.25 (m, 2, OCH_2); IR ($CDCl_3$) 2955, 1735 (C=O), 1669 (C=N), 1438, 1245 cm^{-1}. Anal. ($C_8H_{13}NO_3$) C, H, N.

Reaction of *N*-Allylaniline with Acetonitrile To Give 19 and 20. The mixture of **1** (133.2 mg, 0.30 mmol) and substrate (42 mg, 0.31 mmol) in acetonitrile was stirred at 25 °C under Ar for 6 h as shown in the General procedure. The resulting amber homogeneous solution was stirred with MeOH (3 mL) under CO for 18 h. The normal isolation gave a yellow oil. Purification (column chromatography alumina, 10 mm × 15 cm, hexane:EtOAc = 8:1 ~ 4:1 ~ EtOAc ~ EtOAc/MeOH) gave 13 mg (26%) of **20** as a colorless oil and 28 mg (39%) of **19** as a yellow oil.

19: R_f 0 (alumina, hexane:EtOAc = 4:1), R_f 0.15 (alumina, EtOAc); ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.03 (s, 3, CH_3—C=N), 2.52 (dd, 1, CH_2COOCH_3, J_1 = 16.0, J_2 = 8.9 Hz), 2.83 (dd, 1, CH_2COOCH_3, J_1 = 16.0, J_2 = 5.3 Hz), 3.58 (t, 1, NCH_2CH, J = 9 Hz), 3.70 (s, 3, OCH_3), 4.05 (t, 1, one of NCH_2CH, J = 9 Hz), 4.38 (m, 1, =NCH), 7.05–7.40 (m, 5); IR ($CDCl_3$) 2955, 1738 (C=O), 1600 (C=N), 1500, 1400 cm^{-1}. Anal. ($C_{13}H_{16}N_2O_2$) C, H, N.

20. R_f 0.15 (alumina, hexane:EtOAc = 4:1) ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.24 (s, 3, CH_3), 2.33 (s, 3, CH_3), 6.72 (s, 1, imidazole ring-H), 7.25–7.28 (m, 2, ArH), 7.38–7.49 (m, 3, ArH); IR ($CDCl_3$) 2945, 1605, (C=N), 1510, 1420 cm^{-1}. Anal. ($C_{11}H_{12}N_2$) C, H, N.

By increasing the time of reaction prior to CO exposure, the yield of **19** could be increased at the expense of **20**.

Reaction of *N*-Allyl-2,5-dimethoxyanilline 19 with Acetonitrile To Give 21 and 22. The mixture of **1** (133.2 mg, 0.30 mmol) and substrate (63 mg, 0.32 mmol) was stirred at room temperature under Ar for 8 h. The resulting reddish amber solution was stirred with MeOH (3 mL) under CO for 16 h. The filtration of the mixture through Celite gave a reddish purple solution. Isolation gave a yellow oil, which was separated by the alumina column (hexane:EtOAc = 8:1 ~ 4:1 ~ 1:1 ~ EtOAc ~ EtOAc/MeOH) to give 21 mg (24%) of **22** as a yellow oil and 15 mg (22%) of **21** as a yellow oil, as well as 6 mg (13%) of dimethoxyaniline a colorless crystal.

21: R_f 0.13 (alumina, hexane:EtOAc = 4:1), R_f 0.51 (alumina, EtOAc); ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.18 (s, 3, CH_3CN=N), 2.22 (d, 3, CH=C—CH_3, J = 1 Hz), 3.72 (s, 3, OCH_3), 3.76 (s, 3, OCH_3), 6.60 (d, 1, N—CH=C, J = 1 Hz), 6.75 (d, 1, ArH, J = 2 Hz), 6.91–6.93 (m, 2, ArH); IR (neat) 2938, 2841, 1701, 1623, 1598, 1510, 1399, 1277, 1045 cm^{-1}. Anal. ($C_{13}H_{16}N_2O_2$) C, H, N.

22: R_f 0 (alumina, hexane:EtOAc = 4:1), R_f 0.18 (alumina, EtOAc); ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.76 (s, 3, CH_3—C=N), 2.49 (dd, 1, CH_2COOMe, J_1 = 15.9, J_2 = 8.9 Hz), 2.82 (dd, 1, CH_2COOMe, J_1 = 15.9, J_2 = 8.5 Hz), 3.37 (t, 1, N—CH_2, J = 9 Hz), 3.67 (s, 3, $COOCH_3$), 3.74 (s, 3, OCH_3), 3.75 (s, 3, OCH_3), 3.89 (t, 1, N—CH_2, J = 9 Hz), 4.38 (m, 1, =N—$CHCH_2$), 6.68–6.84 (m, 3, aromatic-H); IR (neat) 2960, 2842, 1742 (C=O), 1612, 1512, 1270, 1215, 1045 cm^{-1}. Anal. ($C_{15}H_{20}N_2O_4$) C, H, N.

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