distortion of the cyclopentadienyl ring are also the same within the uncertainty of these experiments. It is not surprising that many classes of analogous cobalt and rhodium complexes have been prepared. It is also not surprising that different synthetic routes are sometimes required for the preparation of these complexes and that they can have very different chemistries. The excited-state effects evidenced here in the shifts of the predominantly metal valence ionizations can have substantial consequences for oxidation and reduction processes, as well as the stability of key intermediates and products. In these complexes it is clear that delocalization of the highest occupied orbital into the carbonyls is having a significant influence on the character and stability of the first ionization level.

Acknowledgment. We gratefully acknowledge the Department of Energy (Contract DE-AC02, 80ER10746) and the University of Arizona for partial support of this research. D.L.L. is an Alfred P. Sloan Fellow.

Registry No. $CpCo(CO)_2$, 12078-25-0; $CpRh(CO)_2$, 12192-97-1; $Cp^*Co(CO)_2$, 12129-77-0; $Cp^*Rh(CO)_2$, 32627-01-3.

Concerted [4π + 2π] Cycloaddition of $(\eta^5\text{-}C_5H_5)Fe(CO)_2(\eta^1\text{-}C_5H_5)$ with the Isomeric 2-Butenedinitriles

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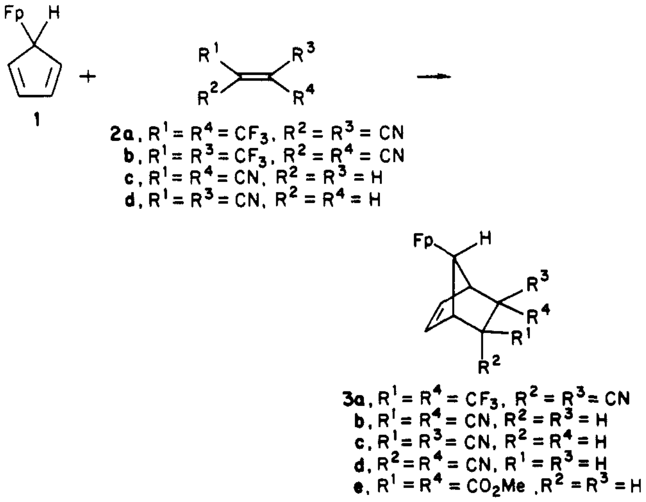
Fumaronitrile and maleonitrile rapidly cycloadd to $(\eta^5\text{-}C_5H_5)Fe(CO)_2(\eta^1\text{-}C_5H_5)$ with comparable rates to afford 7-*syn*-[$(\eta^5\text{-}C_5H_5)Fe(CO)_2$]bicyclo[2.2.1]hept-5-ene-2-*exo*,3-*endo*-dicarbonitrile (**3b**) and a 1:1 mixture of 7-*syn*-[$(\eta^5\text{-}C_5H_5)Fe(CO)_2$]bicyclo[2.2.1]hept-5-ene-2-*exo*,3-*exo*-dicarbonitrile (**3c**) and 7-*syn*-[$(\eta^5\text{-}C_5H_5)Fe(CO)_2$]bicyclo[2.2.1]hept-5-ene-2-*endo*,3-*endo*-dicarbonitrile (**3d**), respectively, in excellent yield. Mechanistic studies strongly support a concerted [4π + 2π] cycloaddition for these reactions.

Introduction

Cycloaddition of transition-metal η^1-allyl complexes to unsaturated electrophilic molecules has been much studied recently.[1] Correlation of the stereochemistry of the starting alkene with the stereochemistry of the product can provide mechanistic insight into this reaction. Williams and Wojcicki[2] reported that $Fp(\eta^1\text{-}C_5H_5)$ (**1**), where Fp = $(\eta^5\text{-}C_5H_5)Fe(CO)_2$, reacts with both *trans*- and *cis*-1,2-bis(trifluoromethyl)-1,2-dicyanoethylene, **2a** and **2b**, respectively, to give the same cycloadduct **3a** in which the trifluoromethyl groups are trans to each other. Fumaronitrile **2c** also yields a 1:1 cycloadduct with undetermined stereochemistry.[2] This paper reports the stereochemistry of the cycloadducts obtained by reaction of fumaronitrile and its geometric isomer maleonitrile **2d** with $Fp(\eta^1\text{-}C_5H_5)$ and the mechanism for these reactions.



1

2a, $R^1 = R^4 = CF_3$, $R^2 = R^3 = CN$
b, $R^1 = R^3 = CF_3$, $R^2 = R^4 = CN$
c, $R^1 = R^4 = CN$, $R^2 = R^3 = H$
d, $R^1 = R^3 = CN$, $R^2 = R^4 = H$

3a, $R^1 = R^4 = CF_3$, $R^2 = R^3 = CN$
b, $R^1 = R^4 = CN$, $R^2 = R^3 = H$
c, $R^1 = R^3 = CN$, $R^2 = R^4 = H$
d, $R^2 = R^4 = CN$, $R^1 = R^3 = H$
e, $R^1 = R^4 = CO_2Me$, $R^2 = R^3 = H$

Results and Discussion

As reported by Williams and Wojcicki,[2] fumaronitrile and $Fp(\eta^1\text{-}C_5H_5)$[3] rapidly react at room temperature. After chromatography, analytically pure cycloadduct is obtained in 85% yield. The IR and ^1H NMR spectra of this compound agree with the data previously reported. Especially instructive for assigning the stereochemistry of this cycloadduct as **3b** is analysis of its ^1H NMR spectrum at 250 MHz.[4] The key absorptions are at δ 3.04 (dd, 1, J = 3.8, 3.9 Hz) and 2.55 (d, 1, J = 3.8 Hz) that are assigned to the *exo*- and *endo*-CHCN protons, respectively. Double irradiation demonstrates that they are coupled to each other (J = 3.8 Hz), and the upfield signal due to the endo hydrogen atom is not coupled to the adjacent bridgehead proton whereas the downfield resonance due to the exo-hydrogen atom is (J = 3.9 Hz).

Surprisingly, maleonitrile[5] rapidly reacts with $Fp(\eta^1\text{-}C_5H_5)$ at room temperature. Indeed, allowing maleonitrile and fumaronitrile to compete for $Fp(\eta^1\text{-}C_5H_5)$ reveals the two alkenes to be of comparable reactivity. This dramatically contrasts with the results with dimethyl fumarate

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(1) (a) Rosenblum, M. *Acc. Chem. Res.* **1974**, *7*, 122. (b) Wojcicki, A. *Ann. N. Y. Acad. Sci.* **1974**, *239*, 100. (c) Cutler, A.; Ehnholt, D.; Lennon, P.; Nicholas, K.; Marten, D. F.; Madhavarao, M.; Raghu, S.; Rosan, A.; Rosenblum, M. *J. Am. Chem. Soc.* **1975**, *97*, 3149. (d) Cutler, A.; Ehnholt, D.; Giering, W. P.; Lennon, P.; Raghu, S.; Rosan, A.; Rosenblum, M.; Tancrede, J.; Wells, D. *Ibid.* **1976**, *98*, 3495. (e) Williams, J. P.; Wojcicki, A. *Inorg. Chem.* **1977**, *16*, 2506.

(2) Williams, J. P.; Wojcicki, A. *Inorg. Chem.* **1977**, *16*, 3116.

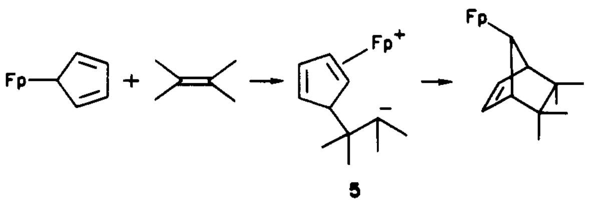
(3) Wilkinson, G.; Piper, T. S. *J. Inorg. Nucl. Chem.* **1956**, *2*, 32.

(4) Davis, J. C.; Van Auken, T. V. *J. Am. Chem. Soc.* **1965**, *87*, 3900.

(5) Ficken, G. E.; Linstead, R. P.; Stephen, E.; Whalley, M. *J. Chem. Soc.* **1958**, 3879.

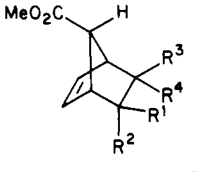
0276-7333/84/2303-1630$01.50/0

Scheme I



and dimethyl maleate.[6,7] Reaction of Fp(η^1-C_5H_5) with dimethyl fumarate occurs rapidly at room temperature whereas no reaction is detected with dimethyl maleate in the absence of diethylchloroalane. Furthermore, Fp(η^1-C_5H_5) and maleonitrile form a 1:1 mixture of cycloadducts in 90% combined yield after purification. These cycloadducts are easily separated by column chromatography on deactivated alumina (activity grade III). Elemental analysis and IR and ^{1}H NMR spectroscopy reveal them to be cycloadducts isomeric with **3b**. Base-catalyzed equilibration of each of these cycloadducts separately provides predominately **3b**[8] that is isolated in high yield (90–94%) after purification. This result shows that all three compounds are isomeric at C(2) and C(3). Detailed analysis of the ^{1}H NMR spectra at 250 MHz of the cycloadducts from maleonitrile and Fp(η^1-C_5H_5) permits their assignment as 2-*exo*,3-*exo*-**3c**, in which the absorptions due to C(2-endo) and C(3-endo) hydrogen atoms occur as a sharp singlet at δ 2.69, and 2-*endo*,3-*endo*-**3d**, in which the resonances of C(2-exo) and C(3-exo) hydrogen atoms appear as a multiplet in which there is coupling to the bridgehead hydrogen atoms as shown by double irradiation experiments at δ 3.15.[4]

The structural assignments of the cycloadducts obtained from Fp(η^1-C_5H_5) and fumaronitrile and maleonitrile are further supported by the properties of their corresponding oxidation products. Oxidation[6,9] of each of the cycloadducts **3b**, **3c**, and **3d** separately with ammonium cerium(IV) nitrate in methanol saturated with carbon monoxide provided esters **4a**, **4b**, and **4c** in 61, 72, and 69% yields, respectively, after purification. The elemental analysis and IR and ^{1}H NMR spectra of these compounds support the structural assignments.



4a, $R^1 = R^4 = CN$, $R^2 = R^3 = H$
b, $R^1 = R^3 = CN$, $R^2 = R^4 = H$
c, $R^2 = R^4 = CN$, $R^1 = R^3 = H$

The striking results reported in this paper have important mechanistic implications. Cycloaddition of transition-metal η^1-allyl complexes to unsaturated electrophilic molecules is believed to occur by a two-step [3 + 2] mechanism.[1a–c,2,9] Analogous reaction of metal η^1-cyclopentadienyl complexes with electrophilic alkenes is shown in Scheme I. Zwitterion **5** is formed as an intermediate that cyclizes with overall 1,2-metal migration. The doubly bonded carbon atoms of the starting alkene are singly bonded in zwitterion **5**. The stereochemistry of the starting alkene may be lost if rotation about this single bond is fast relative to cyclization. Thus, reaction of both *trans*- and *cis*-1,2-bis(trifluoromethyl)-1,2-dicyanoethylene with Fp(η^1-C_5H_5) affords the same trans cycloadduct **3a**. Addition of dimethyl maleate to Fp(η^1-C_5H_5) in the presence of diethylchloroalane affords cycloadduct **3e** in which the ester groups are trans to each other. Both of these results can be explained by two-step [3 + 2] cycloaddition in which there is isomerization in the intermediary zwitterion. However, Williams and Wojcicki[2] propose an additional possibility. If the cis isomer only slowly cycloadds relative to the trans isomer, then the cis isomer may isomerize to the trans isomer that rapidly cycloadds. Therefore, the trans stereochemistry in the cycloadduct does not distinguish a two-step [3 + 2] cycloaddition from a concerted [4 + 2] cycloaddition. Clearly, the retention of alkene stereochemistry that we observe with the isomeric butenedinitriles precludes two-step [3 + 2] cycloaddition in which there is time for rotation about the carbon–carbon single bond in zwitterion **5**. Our results require that cyclization is fast in zwitterion **5** relative to rotation about the carbon–carbon single bond (electrostatic interactions in the zwitterion could disfavor rotation relative to cyclization)[10] or the cycloaddition is concerted. To distinguish these two possibilities, the rate of reaction of Fp(η^1-C_5H_5) with excess maleonitrile in solvents of very different polarity was determined. The relative rates in benzene, dichloromethane, and methanol were 1:2:4, respectively, under comparable conditions. This small difference in relative rates and the observation that methanol did not trap an intermediary zwitterion strongly suggest that this reaction occurs by a concerted [$4\pi + 2\pi$] cycloaddition.

Although the relative rates of reaction in these solvents were comparable there was a dramatic dependence of the exo:endo product ratio on solvent. The ratios of **3c**:**3d** were 6:1, 1:1, and 1:2 in benzene, dichloromethane, and methanol, respectively. Although solvent dependence on the stereoselectivity of the Diels–Alder reaction has been reported[11] the effect was smaller than that observed here. Depending on solvent the Alder "endo rule" is obeyed (in methanol) or flagrantly violated (in benzene).[12,13]

Experimental Section

All reactions were carried out by using standard Schlenk techniques under an atmosphere of argon or purified nitrogen. Solvents were routinely dried by standard procedures[15] and stored under an inert atmosphere. NMR solvents were predried over 3-Å molecular sieves, subjected to three freeze–thaw–pump cycles, and stored under an inert atmosphere.

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[6] Wright, M. E. *Organometallics* **1983**, *2*, 558. Wright, M. E.; Hoover, J. F.; Nelson, G. O.; Scott, C. P.; Glass, R. S. *J. Org. Chem.*, in press.

[7] Maleonitrile, fumaronitrile, and dimethyl fumarate have comparable reactivity as dienophiles with cyclopentadiene in dioxane, whereas dimethyl maleate is 100 times less reactive under these conditions: Sauer, J.; Wiest, H.; Mielert, A. *Chem. Ber.* **1964**, *97*, 3183.

[8] At equilibrium in *tert*-butyl alcohol at 30 °C the ratio of **3b**:**3c**:**3d** is 10:1:3. Each of the pure isomers is rapidly isomerized to this equilibrium with potassium *tert*-butoxide in *tert*-butyl alcohol.

[9] Lennon, P.; Rosan, A. M.; Rosenblum, M. *J. Am. Chem. Soc.* **1977**, *99*, 8426.

[10] Giering, W. P.; Rosenblum, M. *J. Am. Chem. Soc.* **1971**, *93*, 5299. Su, S. R.; Wojcicki, A. *Inorg. Chim. Acta* **1974**, *8*, 55. Chen, L. S.; Su, S. R.; Wojcicki, A. *Ibid.* **1978**, *27*, 79.

[11] Berson, J. A.; Hamlet, Z.; Mueller, W. A. *J. Am. Chem. Soc.* **1962**, *84*, 297.

[12] Carruthers, W. "Some Modern Methods of Organic Synthesis", 2nd ed.; Cambridge University Press: Cambridge, 1978; pp 204–211. Maleonitrile and cyclopentadiene at 40 °C without solvent give bicyclo[2.2.1]hept-5-ene-2-*endo*,3-*endo*-dicarbonitrile in 94% yield: Blomquist, A. T.; Winslow, E. C. *J. Org. Chem.* **1945**, *10*, 149. In dioxane at 20 °C maleonitrile and cyclopentadiene produce a 76:24 mixture of bicyclo[2.2.1]hept-5-ene-2-*endo*,3-*endo*-dicarbonitrile and bicyclo[2.2.1]hept-5-ene-2-*exo*,3-*exo*-dicarbonitrile.[7]

[13] Dramatic changes in product ratios are also well-known in Diels-Alder reactions in which there is a change from kinetic to thermodynamic control, e.g., in the cycloaddition of furan and maleic anhydride.[14]

[14] Carruthers, W. "Some Modern Methods of Organic Synthesis", 2nd ed.; Cambridge University Press: Cambridge, 1978; p 191.

[15] Gordon, A. J.; Ford, R. A. In "The Chemists Companion"; Wiley: New York, 1972; p 429–447.

Spectroscopic measurements utilized the following instrumentation: ^{1}H NMR, Varian EM360, Bruker WM-250 (at 250 MHz); IR, Perkin-Elmer 983; UV-vis, IBM 9420. NMR chemical shifts reported in δ units vs. internal tetramethylsilane. Samples for NMR spectroscopy were passed through a Celite plug contained in a disposable pipet to remove finely divided decomposition particles and allow optimum spectroscopic resolution.

Fp(η^1-C_5H_5) (1)[3] and maleonitrile (2d)[5] were prepared by literature methods. Fumaronitrile was obtained from Monsanto Chemical Co. (St. Louis, MO) and recrystallized from diethyl ether–hexanes prior to use.

Preparation of 7-*syn*-[(η^5-C_5H_5)Fe(CO)$_2$]bicyclo[2.2.1]hept-5-ene-2-*exo*,3-*exo*-dicarbonitrile (3c) and 7-*syn*-[(η^5-C_5H_5)Fe(CO)$_2$]bicyclo[2.2.1]hept-5-ene-2-*endo*,3-*endo*-dicarbonitrile (3d). To a stirred solution of Fp(η^1-C_5H_5) (1, 0.24 g, 1.0 mmol) in benzene, dichloromethane, or methanol (20 mL) at 0 °C was added a solution of maleonitrile (0.086 g, 1.1 mmol) in the same solvent (5 mL). The reaction was allowed to warm to room temperature and was stirred for 1 h. The solvent was removed under reduced pressure, and the residue was column chromatographed on alumina of activity grade III. Initial elution with hexanes gave ferrocene. Elution with 3:1 (v/v) hexanes–dichloromethane gave **3c** as a yellow solid. Further elution with 3:1 (v/v) dichloromethane–hexanes gave **3d** as a yellow solid. The yields of products in each of the solvents were as follows: benzene, **3c** (0.245 g, 77%) and **3d** (0.043 g, 13%); dichloromethane, **3c** (0.156 g, 49%) and **3d** (0.144 g, 45%); methanol, **3c** (0.107 g, 33%) and **3d** (0.191 g, 60%). The spectroscopic parameters and elemental microanalyses for each of these compounds are as follows:

3c: ^{1}H NMR ($CDCl_3$, 250 MHz) δ 6.08 (m, 2, H5, H6), 4.77 (s, 5, C_5H_5), 3.20 (m, 2, H1, H4), 2.88 (m, 1, H7-anti), 2.69 (s, 2, H2-endo, H3-endo); IR (KBr) 2240, 2234 (C≡N), 2003, 1943 (CO) cm^{-1}; UV–vis (benzene) 351 nm (866). Anal. Calcd for $C_{16}H_{12}FeN_2O_2$: C, 60.03; H, 3.78. Found: C, 60.08; H, 3.85.

3d: ^{1}H NMR ($CDCl_3$, 250 MHz) δ 6.37 (m, 2, H5, H6), 4.70 (s, 5, C_5H_5), 3.22 (m, 2, H1, H4), 3.15 (m, 2, H2-exo, H3-exo), 2.18 (m, 1, H7-anti); IR (KBr) 2241, 2236 (C≡N), 2004, 1947 (CO) cm^{-1}; UV–vis (benzene) 351 nm (866). Anal. Calcd for $C_{16}H_{12}FeN_2O_2$: C, 60.03; H, 3.78. Found: C, 60.17; H, 3.89.

Preparation of 7-*syn*-[(η^5-C_5H_5)Fe(CO)$_2$]bicyclo[2.2.1]hept-5-ene-2-*exo*,3-*endo*-dicarbonitrile (3b). Complex **3b** was prepared from Fp(η^1-C_5H_5) (**1**, 0.24 g, 1.0 mmol) and fumaronitrile (**2c**, 0.086 g, 1.1 mmol) in dichloromethane by using the same procedure as that for synthesizing **3c**/**3d**. The reaction mixture was purified by column chromatography on alumina of activity grade III. Elution with hexanes gave ferrocene. Further elution with 1:1 (v/v) hexanes–dichloromethane gave **3b** as a yellow solid (0.272 g, 85%). The ^{1}H NMR (60 MHz) spectrum of this material was identical with that reported[2] for **3b**. The carbonyl and nitrile stretching frequencies in the IR for this material were also the same as those reported[2] for **3b**. The spectroscopic data for the sample of **3b** synthesized as above is: ^{1}H NMR ($CDCl_3$, 250 MHz) δ 6.25 (m, 2, H5, H6), 4.74 (s, 5, C_5H_5), 3.25 (m, 1, H4), 3.20 (m, 1, H1), 3.04 (dd, 1, J = 3.9, 3.8 Hz, H3-exo), 2.60 (m, 1, H7-anti), 2.55 (d, 1, J = 3.8 Hz, H2-endo).

Competitive Reaction of Fumaronitrile (2c) and Maleonitrile (2d) with Fp(η^1-C_5H_5) (1). Fumaronitrile (13 mg, 0.17 mmol), maleonitrile (13 mg, 0.17 mmol), and deuteriochloroform (0.5 mL containing 1% tetramethylsilane) were combined in an NMR tube. To this solution was added Fp(η^1-C_5H_5) (41 mg, 0.17 mmol) in deuteriochloroform (0.2 mL) with agitation to obtain rapid mixing. ^{1}H NMR spectroscopic analysis at 250 MHz after 1 h showed the ratio of **3b**:**3c**/**3d** to be 1.17:1.00 with no observable Fp(η^1-C_5H_5) left in solution.

Equilibration of 3a, 3b, and 3c. To a solution of **3b** (20 mg, 0.06 mmol) in *tert*-butyl alcohol (1 mL) at 30 °C was added potassium *tert*-butoxide (8 mg, 0.06 mmol). The reaction mixture was stirred for 45 min. The solution was then cooled to 0 °C, neutralized with dilute aqueous hydrochloric acid solution, and extracted with diethyl ether. Removal of the diethyl ether gave a yellow-orange solid shown by ^{1}H NMR spectroscopic analysis at 250 MHz to consist of **3b**, **3c**, and **3d** in the ratio of 10:1:3, respectively. This isomeric mixture was separated by column chromatography on alumina of activity grade III. Elution with 7:3 (v/v) hexanes–dichloromethane gave products whose ^{1}H NMR and IR spectra were identical with those of authentic samples.

Compounds **3c** and **3d** gave identical isomeric mixtures when subjected to the reactions conditions given for **3b**.

Kinetic Measurements of the Reaction of 1 with 2d. The absorption maxima and extinction coefficients for **1**, **3c**, and **3d** between 300 and 800 nm were determined to be 322 (7774), 351 (866), and 351 nm (866), respectively. All reactions were conveniently monitored at 322 nm. The reactions were studied under pseudo-first-order conditions by using a large excess of olefin. Pseudo-first-order rate constants, k_{obsd}, were calculated from the slopes of plots of ln $[(A_t - A_\infty)/(A_0 - A_\infty)]$ vs. time. All of the reactions obeyed first-order kinetics for at least 3 half-lives. All reactions were run at the following initial concentrations: **1**, 1.33 × 10^{-3} M (±5%); **2d**, 2.1 × 10^{-2} M (±5%), using a 1.0-mm quartz cell at 23.3 ± 0.5 °C. Three separate runs with each solvent studied were performed, giving an average reproducibility of ±8%. The observed rates in each solvent were as follows: benzene, 3.8 × 10^{-4} s^{-1}; dichloromethane, 7.3 × 10^{-4} s^{-1}; methanol, 16 × 10^{-4} s^{-1}.

Preparation of 7-*syn*-Carbomethoxybicyclo[2.2.1]hept-5-ene-2-*exo*,3-*endo*-dicarbonitrile (4a). To a stirred solution of **3b** (0.24 g, 0.75 mmol) in methanol (15 mL) saturated with carbon monoxide at 0 °C was added ammonium cerium(IV) nitrate (2.5 g, 4.5 mmol). The reaction mixture was allowed to stir for 1 h at 0 °C and 1 h at room temperature with carbon monoxide bubbling through the solution. The methanol was then removed under reduced pressure. The resultant solid was dissolved in water and extracted with dichloromethane (5 × 30 mL). Removal of the dichloromethane after the solution was dried with anhydrous magnesium sulfate gave crude **4a**. Distillation (80 °C, 0.5 mm) from bulb to bulb gave **4a** as a clear oil (90 mg, 60%). A sample was purified by gas chromatography on a 0.25 in. × 5 ft 10% SE-30 on Chromosorb W column at 200 °C: ^{1}H NMR ($CDCl_3$, 250 MHz) δ 6.36 (dd, 2, J = 1.9, 1.8 Hz, H5, H6), 3.69 (dd, 1, J = 3.4, 1.7 Hz, H4), 3.66 (m, 1, H1), 3.64 (s, 3, CH_3), 3.26 (dd, 1, J = 4.2, 3.4 Hz, H3-exo), 2.90 (m, 1, H7-anti), 2.55 (d, 1, J = 4.2 Hz, H2-endo); IR (KBr) 2245 (C≡N), 1739 (CO), 1238 cm^{-1}. Anal. Calcd for $C_{11}H_{10}N_2O_2$: C, 65.33; H, 4.99. Found: C, 65.09, H, 5.05.

Preparation of 7-*syn*-Carbomethoxybicyclo[2.2.1]hept-5-ene-2-*exo*,3-*exo*-dicarbonitrile (4b). Complex **3c** (0.32 g, 1.0 mmol) was oxidized to the corresponding ester **4b** as described for the preparation of **4a** from **3b**. Repeated crystallizations of the crude product from dichloromethane–hexanes gave **4b** (0.145 g, 72%): mp 114–115.5 °C dec; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 6.23 (ddd, 2, J = 2.2, 1.8, 0.5 Hz, H5, H6), 3.69 (dd, 2, J = 2.2, 1.8 Hz, H1, H4), 3.65 (s, 3, CH_3), 3.18 (m, 1, H7-anti), 2.73 (s, 2, H2-endo, H3-endo); IR (KBr) 2242 (C≡N), 1744, 1216 (CO) cm^{-1}. Anal. Calcd for $C_{11}H_{10}N_2O_2$: C, 65.33; H, 4.99. Found: C, 65.41; H, 5.03.

Preparation of 7-*syn*-Carbomethoxybicyclo[2.2.1]hept-5-ene-2-*endo*,3-*endo*-dicarbonitrile (4c). Complex **3d** (0.32 g, 1.0 mmol) was oxidized to the corresponding ester **4c** as described for the preparation of **4a** from **3b**. Repeated crystallizations of the crude product from dichloromethane–hexanes gave **4c** (0.14 g, 69%): mp 121–145 °C dec; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 6.49 (m, 2, H5, H6), 3.69 (m, 2, H1, H4), 3.62 (s, 3, CH_3), 3.38 (m, 2, H2-exo, H3-exo), 2.54 (m, 1, H7-anti); IR (KBr) 2250 (C≡N), 1733 (CO) cm^{-1}. Anal. Calcd for $C_{11}H_{10}N_2O_2$: C, 65.33; H, 4.99. Found: C, 65.27; H, 5.06.

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Registry No. 1, 12247-96-0; **2c**, 764-42-1; **2d**, 928-53-0; **3b**, 91796-38-2; **3c**, 91796-39-3; **3d**, 91796-40-6; **4a**, 91711-73-8; **4b**, 91796-41-7; **4c**, 91796-42-8.