

2 H), 1.3 (br m, 16 H), 0.8 (t, 3 H, H-18); MS, m/z 296 (M^+ $C_{18}H_{32}O_3$), 183 ($CHCHCO(CH_2)_6COOH$), 167 ($COCHCH(C-H_2)_7CH_3$), 157 ($CO(CH_2)_6COOH$), 139 ($CHCH(CH_2)_7CH_3$).

trans-10-Oxooctadec-8-enoic acid (10): 1H NMR (300 MHz, $CDCl_3$) δ 6.8 (dt, 1 H, H-8), 6.1 (dd, 1 H, H-9), 2.5 (t, 2 H, H-11), 2.3 (t, 2 H, H-2), 2.2 (dt, 2 H, H-7), 1.6 (br m, 2 H), 1.4 (br m, 2 H), 1.3 (br m, 16 H), 0.8 (t, 3 H, H-18); ^{13}C NMR (300 MHz, $CDCl_3$) δ 200.8 (C-10), 178.3 (COOH), 146.9 (C-8), 130.3 (C-9), 40.2, 33.8, 32.4, 31.9, 29.5, 29.4, 29.2, 29.1, 28.8, 27.9, 24.6, 24.4, 22.7, 14.2 (CH_3); UV δ_{max} 223 and 276 nm; MS, m/z 296 (M^+ $C_{18}H_{32}O_3$), 183 ($COCHCH(CH_2)_6CH_3$), 167 ($CHCHCO(CH_2)_7CH_3$), 155 ($CHCH(CH_2)_6COOH$), 141 ($CO(CH_2)_7CH_3$).

Rearrangement of ^{18}O -Labeled 5 and 6 under $^{32}O_2$. The following procedure was used with each hydroperoxyoctadecenoic acid. The purified ^{18}O -labeled hydroperoxyoctadecenoic acids (100 mg, 2.9×10^{-4} mol) and DTBN (5 mg) were dissolved in 10 mL of hexane and placed into a flask fitted with a vacuum-stoppered catch flask with condensing sidearm.

The apparatus was filled with $^{18}O_2$ gas through the upper vacuum stopcock, with the lower stopcock open. The system was closed off, and the reaction flask was immersed in a 40 °C constant

temperature oil bath. After 5 h, the gaseous O_2 in the system was condensed into the condensing sidearm (liquid N_2) of the catch flask, and the reaction mixture was allowed to cool to room temperature. The catch flask's vacuum stopcock was closed after 15 min. The hexane was removed in vacuo, and the hydroperoxyoctadecenoic acids were converted to the oxooctadecenoic acids by treatment with pyridine/acetyl chloride. The oxooctadecenoic acids were purified by preparative TLC, separated by semipreparative RP-HPLC, and analyzed for their incorporation level by direct-probe low-resolution mass spectroscopy. The recovered gas samples were analyzed for $^{16}O_2$ vs $^{18}O_2$ via the same mass spectroscopic technique.

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Registry No. 5, 110551-46-7; 5- $^{18}O_2$, 110551-47-8; 6, 96963-17-6; 6- $^{18}O_2$, 110551-48-9; 7, 99640-09-2; 7-ol, 110567-68-5; 7 (peroxide), 110551-49-0; 8, 99640-11-6; 8-ol, 110657-92-6; 9, 99640-10-5; 10, 99640-12-7; oleic acid, 112-80-1; di-*tert*-butyl hyponitrite, 14976-54-6.

Cobalt-Catalyzed Reaction of Nitric Oxide with Aryl-Substituted Olefins in the Presence of Tetrahydroborate Ion

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A new transition-metal-catalyzed reaction of nitric oxide with aryl-substituted olefins in the presence of BH_4^- has been reported, where the oximes of alkyl aryl ketones are the products. The most successful results were obtained by using styrene and its ring-substituted derivatives as the substrate and $Co(DH)_2(py)Cl$ as the catalyst. A process involving the intermediate formation of a metal-alkyl complex and its subsequent decomposition to alkyl radical followed by the reaction of the radical with NO was proposed as the reaction mechanism in relation to the already reported cobalt-catalyzed oxygenation of aryl-substituted olefins.

Catalysis by transition-metal complexes is widely used in organic synthesis.¹ Many of them proceed via catalytic activation of small molecules such as hydrogen, carbon monoxide, carbon dioxide, and even molecular oxygen, but little is known about the activation of nitric oxide (NO) in spite of the abundance in the environment.² In the field of coordination chemistry, however, it is known that NO is a versatile ligand which stabilizes both electron-rich and electron-deficient transition-metal complexes by changing its charge distribution and structure.^{2a} Some stoichiometric reaction of NO with organo-transition-metal complexes are known affording alkyl- or arylnitroso-hydroxylamines as the main products.³ Recently, insertion of (or ligand migration to) coordinated NO leading to the formation of nitrogen-carbon bond as well as mono-

nitrosation of organic groups to nitroso compounds, oximes, or nitriles have been reported.^{4,5}

Nevertheless, no catalytic reaction involving NO has been reported⁶ probably because the coordination abilities of insertion products are too high for replacing them by either NO or the organic substrates, a process necessary for ensuring the catalytic cycle.

In this report we describe a new transition-metal-catalyzed reaction of NO with aryl-substituted olefins in the presence of BH_4^- and bis(dimethylglyoximate)cobalt as the catalyst.⁶ The products obtained were the oximes of alkyl aryl ketones. Although the isolated yields of oximes based on the used substrates were moderate, this is the first example of transition-metal-catalyzed organic synthesis utilizing NO (eq 1). The cobalt-catalyzed oxygenation⁷ of

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(6) A preliminary communication of this article was published: Okamoto, T.; Oka, S. *J. Chem. Soc., Chem. Commun.* 1984, 289.




(7) Okamoto, T.; Oka, S. *J. Org. Chem.* 1984, 49, 1589.

Table I. Nitrosation of Styrene and Its Ring-Substituted Derivatives

entry	RC ₆ H ₄ CH=CH ₂ , R	equiv of Co(DH) ₂ (py)Cl/ substrt	reducing agent (equiv/substrt)	reactn time, h	isoltd yield of RC ₆ H ₄ C(CH ₃)=NOH, %
1 ^a	H	0.20	TEA (1.0)	24	53
2	H	0.20	TEA (1.0)	32	68
3	H	0.25	TBA (0.5)	37	30
4 ^b	H	0.13	TEA (1.0)	23	4
5	<i>o</i> -Cl	0.20	TEA (1.0)	24	68
6	<i>p</i> -Cl	0.20	TEA (1.0)	22	69
7	<i>p</i> -Cl	0.30	TEA (1.0)	22	67
8	<i>p</i> -Cl	0.20	TBA (1.0)	30	61
9	<i>o</i> -Br	0.20	TEA (1.0)	24	60
10	<i>o</i> -CH ₃	0.20	TEA (1.0)	30	37
11	<i>p</i> -CH ₃	0.20	TEA (1.0)	35	68
12	<i>p</i> -CH ₃	0.20	TBA (1.0)	37	43
13	<i>m</i> -NO ₂	0.20	TEA (1.0)	30	41
14	<i>p</i> -CH ₃ O	0.20	TEA (1.0)	38	55
15	<i>o</i> -CH=CH ₂	0.25	TEA (1.0)	30	36
16	<i>o</i> -OCH ₂ CH=CH ₂	0.20	TEA (1.0)	36	33 ^c

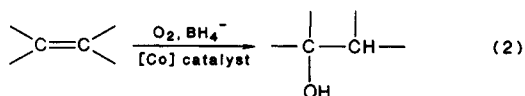
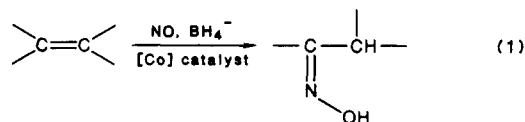
^a β -Methylstyrene, *cis*-stilbene, *trans*-stilbene, and 1,1-diphenylethylene, all of which are considered to be α - or β -substituted derivatives of styrene, were unreactive and recovered unchanged except for β -methylstyrene. ^b Catalyst: (phthalocyanin)cobalt. ^c Isolated yield based on the consumed substrate was 94%.

Table II. Nitrosation of Several Aryl-Substituted Olefins Other than Styrene and Its Ring-Substituted Derivatives

entry	substrt	equiv of Co(DH) ₂ (py)Cl/ substrt	reducing agent (equiv/substrt)	reactn time, h	product	isoltd yield, %
1 ^a	PhCH=CHCH=CH ₂	0.20	TEA (1.0)	38	PhCH=CHC(CH ₃)=NOH	63
2	PhCH=CHCH ₂ OH	0.20	TEA (1.0)	40	PhC(=NOH)CH ₂ CH ₂ OH	9 ^b
3 ^c	<i>trans</i> -PhCH=CHCO ₂ Me	0.20	TEA (1.0)	40		0
4		0.20	TEA (1.0)	36		45
5		0.25	TEA (1.0)	35		0
6	PhSOCH=CH ₂	0.20	TEA (1.0)	36		0
7	PhC≡CH	0.20	TEA (1.0)	48	PhC(CH ₃)=NOH CH ₂ =C(Ph)Co(DH) ₂ (py)	8 29 ^d
8	PhCH(Br)CH ₃	0.25	TBA (0.5)	37	PhC(CH ₃)=NOH	19
9	PhCH(Br)CH ₃	0.20	TEA (1.0)	36	PhC(CH ₃)=NOH	28
10	PhCH=CHCH ₂ Br	0.20	TEA (1.0)	36	PhCH=CHCH=NOH	28
11 ^e	CH ₃ CH(Ph)Co(DH) ₂ (py)		TEA (1.0)	5	PhC(CH ₃)=NOH PhCH=CH ₂	24.4 ^f 23.7 ^f
12 ^e	CH ₃ CH(Ph)Co(DH) ₂ (py)			5	PhC(CH ₃)=NOH PhCH=CH ₂ Co(DH) ₂ (py)NO ₂	4 ^f 27 ^f >63

^a 1,4-Diphenyl-1,3-butadiene was unreactive. ^b Isolated yield based on the consumed substrate was 27%. ^c Cinnamitrile was unreactive and recovered unchanged. ^d Isolated yield based on the catalyst used. ^e Stoichiometric reaction of the organocobalt complex. ^f Determined by gas chromatography using diphenyl ether as an internal standard.

aryl-substituted olefins by molecular oxygen and BH₄⁻ is a known reaction (eq 2).



Results and Discussion

When a mixture of an aryl-substituted olefin and BH₄⁻ was stirred under NO atmosphere in the presence of cobalt complex at room temperature, the corresponding oxime of alkyl aryl ketone was isolated as the main product after the usual workup procedure followed by chromatographic separation on silica gel. The reaction was completely regioselective for all substrates examined; the other regio-

somers were not formed. The results with various aryl-substituted olefins are summarized in Tables I and II. In most cases in these tables, 0.2 equiv of Co(DH)₂(py)Cl (DH₂ = dimethylglyoxime, py = pyridine) per substrate was used. Increasing the amount of catalyst to 0.3 equiv had no effect on the final result (entries 6 and 7 in Table I). On the other hand, the use of less than 0.2 equiv of the catalyst brought about a significant lowering in the yield of oxime, suggesting that the overall turnover of catalyst is about five under the present reaction conditions. Tetraethylammonium tetrahydroborate (TEA) was slightly more effective than tetrabutylammonium tetrahydroborate (TBA) (see entries 7, 8, 11, and 12 in Table I). The use of less than 1.0 equiv of the reducing agent per substrate afforded the lower yield of oxime (entry 3 in Table I and entry 8 in Table II). Furthermore, nitrosation of styrene or *p*-chlorostyrene did not proceed in the presence of Zn powder (20–30 equiv per substrate, in methanol or *N,N*-dimethylformamide–methanol) or lithium aluminum tetrahydride (1.0 or more equiv) as the reducing agent even

Table III. Solvent Dependence in the Formation of Acetophenone Oxime from Styrene^a

entry	solvent	reactn time, h	yield of acetophenone oxime, ^b %
1	<i>i</i> -PrOH-MeOCH ₂ CH ₂ OMe (1:1 vol ratio)	24	83
2	(CH ₃) ₂ NCHO	41	57
3	[(CH ₃) ₂ N] ₂ PO	41	52
4	tetrahydrofuran	41	39
5	CH ₃ SOCH ₃	41	20
6	<i>i</i> -PrOH	41	17
7	MeOCH ₂ CH ₂ OMe	41	6
8	MeCN	41	5
9	benzene	41	2

^aReactions were performed as described in the Experimental Section, with 0.87 mmol (0.091 g) of styrene, 0.20 equiv (per styrene) of Co(DH)₂(py)Cl, 1.2 equiv (per styrene) of TEA in 0.4 mL of various solvents, and NO at atmospheric pressure. However, the reaction period was 24 or 41 h. ^bDetermined by gas chromatography using diphenyl ether as an internal standard.

if Co(DH)₂(py)Cl was used as the catalyst. The yield of acetophenone oxime gradually decreased after more than 20 h, indicating further alteration of the oxime under the catalytic reaction conditions. Since oxime is slowly reduced by BH₄⁻, the reduction is probably the major cause for the decrease in yield. When ring-substituted derivatives of styrene were used as the starting substrate, the resulting oximes also can be reduced further. Low yields may also be due to the side reactions related to the known stoichiometric reactions.^{3,8} Especially, further nitrosation of the primary products, nitrosoalkanes, leading to more complex nitrogen compounds might take part in lowering the yields of oximes, because such a process providing nitrosohydroxylamines, azo compounds, and *N*-nitrosoamine oxides from nitroso compounds has been already reported in the stoichiometric reaction of transition-metal-alkyl complexes.³ However, none of the products expected to arise from the above-mentioned side reactions could have been detected. Probably, the silica gel column, which was necessitated for the isolation of products from the catalyst mixture, adsorbed such nitrogen-containing compounds. On the other hand, the side products generated by dimerization and/or hydrogenation of the substrates such as 2,3-diphenylbutane and ethylbenzene, which were identified in the analogous cobalt-catalyzed oxygenation,⁷ were occasionally detected by gas chromatography, depending on the reaction conditions.⁹ However, the unusually small amount of these side products in the reactions in Table I is not sufficient to account for the low yields of oximes.

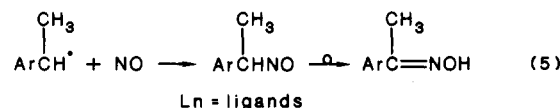
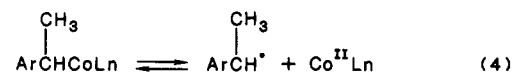
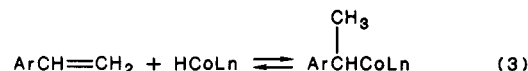
Table III shows the solvent dependence of yields of acetophenone oxime from styrene. In some solvents such as benzene, acetonitrile, and dimethoxyethane, in which the cobaloxime is insoluble, the reaction did not proceed smoothly. As can be seen from the results on the catalyst effect of various cobalt complexes summarized in Table IV, Co(DH)₂(py)Cl is the most effective at least for the nitrosation of styrene. It is notable that Co(TPP) (TPPH₂ = tetraphenylporphyrin) and Co(phthalocyanine), both of which are highly effective catalysts for oxygenation,⁷ did not promote the nitrosation. The catalytic efficiency of Co(DH)₂(H₂O)₂ was dependent on the amount of pyridine

Table IV. Catalyst Dependence in the Formation of Acetophenone Oxime from Styrene^a

entry	catal	equiv of added pyridine/catal	reactn time, h	yield of acetophenone oxime, ^b %
1	Co(DH) ₂ (py)Cl	0	2	34
2	Co(DH) ₂ (H ₂ O) ₂	0	2	5
3	Co(DH) ₂ (H ₂ O) ₂	0.5	2	2
4	Co(DH) ₂ (H ₂ O) ₂	1.0	2	14
5	Co(DH) ₂ (H ₂ O) ₂	2.0	2	8
6	Co(DH) ₂ (H ₂ O) ₂	4.0	2	5
7	Co(salen) ^c	0	2	2
8	Co(sacac) ₂ (en) ^d	0	2	8
9	Co(TPP) ^e	0	2	0

^aReactions were conducted as described in Table III except that 0.20 equiv (per styrene) of various catalysts (and, in some cases, pyridine was added together with the catalyst) was used and that the solvent was always (except for entry 9) 0.2 mL of isopropyl alcohol plus 0.2 mL of 1,2-dimethoxyethane. Also, the reaction period was always 2 h. ^bDetermined by gas chromatography using diphenyl ether as an internal standard. ^cH₂salen = 2,2'-ethylenebis(nitrilomethylidene)diphenol. ^dH₂(sacac)₂(en) = ethylenebis(nitrilo-2-pentylidene-4-thione). ^eTPPH₂ = tetraphenylporphyrin; and in this last case the same volume of *N,N*-dimethylformamide was used instead of isopropyl alcohol plus 1,2-dimethoxyethane.

added. The better yield of acetophenone oxime was obtained when an equimolar amount of pyridine per catalyst was used, suggesting that Co(DH)₂(py) is more effective than Co(DH)₂(py)₂ or Co(DH)₂(H₂O)₂. The low reactivities of the cobalt(II) complexes examined show a clear contrast to their high reactivities in the oxygenation reaction. Since the reaction conditions of both oxygenation and nitrosation are very similar with each other, related mechanism with intermediate formation of cobalt-alkyl complex are expected for both reactions (eq 3-5). The observed des-



crepancy may be reasonable in the light of the higher coordinating ability and larger trans effect of NO ligand¹⁰ as compared with molecular oxygen. This explanation is also supported by the experimental facts that Co(DH)₂NO was isolated as a stable complex¹¹ in the reaction of Co(DH)₂(H₂O)₂ with NO and that the formation of Co(DH)₂(py)NO was confirmed by spectroscopy.^{10a,12}

When CH₃CH(Ph)Co(DH)₂(py), the reactive intermediate postulated in the present reaction using styrene, was treated with NO in the presence of TEA, acetophenone oxime was formed in a yield of 24.4% together with styrene (23.7%) after a reaction period of 5 h (see entry 11 in Table II). This result substantiates the existence of a process involving the formation of intermediate cobalt-alkyl complex in the present catalytic reaction. Because the complex has no vacant coordination site, coordination of NO to the complex may be a difficult process to occur. Probably, the reaction proceeds via the free radical combination of NO

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(9) It is well-known that the hydrogenation was the main reaction by using Co(cyclam)Cl₂ as catalyst. High concentration of catalyst facilitated the dimer formation. Addition of NH₄Cl increased the amounts of dimer and hydrogenation product.

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(12) Troglor, W. C.; Marzilli, L. G. *Inorg. Chem.* 1974, 13, 1008.

with 1-phenylethyl formed from the cobalt-alkyl complex, without participation of a process involving the insertion of coordinated NO to the cobalt-carbon bond. Facile decomposition of cobalt(III)-alkyl complexes into the corresponding alkyl radical and cobalt(II) species has been already confirmed.¹³ The absence of two coordination sites at *cis* positions in the complex might contribute to the successful catalytic reaction by preventing the catalyst poisoning with the reaction product. The finding concerning the stable transition-metal complexes having η^2 -alkyl nitroso ligand^{3b} supports the above explanation. In an analogous catalytic reaction using phenylacetylene instead of styrene (entry 7 in Table II), were isolated acetophenone oxime in a yield of 8% and $\text{CH}_2=\text{C}(\text{Ph})\text{Co}(\text{DH})_2(\text{py})$ ¹⁴ in a yield of 29% (based on the complex used). The structure of the latter compound, which was collected by filtration after the reaction and purified by careful washing with ether, was confirmed by IR and elemental analysis.¹⁵ The successful isolation of such the cobalt-alkenyl complex, which is more stable than the above cobalt-1-phenylethyl complex under the present reaction conditions,¹³ will offer further corroborating evidence for the postulate that, in the reaction with styrene, the corresponding cobalt-alkyl complex is formed.

Stoichiometric reaction of $\text{CH}_3\text{CH}(\text{Ph})\text{Co}(\text{DH})_2(\text{py})$ with NO in the absence of BH_4^- produced acetophenone oxime in a yield of 4% and styrene in a yield of 27% together with $\text{Co}(\text{DH})_2(\text{py})\text{NO}_2$ ¹⁶ (>63%) (entry 12 in Table II). The last compound, which is dark yellow, had begun to precipitate after a reaction period of 30 min. The precipitate was collected by filtration after completion of the reaction prior to the conventional workup procedure and washed with some organic solvents. It was then identified as $\text{Co}(\text{DH})_2(\text{py})\text{NO}_2$ by IR and elemental analysis.¹⁵ The formation of the same precipitate was also observed in the preceding stoichiometric reaction in the presence of BH_4^- (TEA) (entry 11 in Table II) and occasionally in the catalytic reaction, but the amounts were negligible. Apparently, BH_4^- contributes in preventing the formation of nitro complex through undesirable side reactions leading to inactivation of the catalyst used. One of the key steps of successful catalytic nitrosation might be based on such the effect of BH_4^- .

Experimental Section

Materials and Instruments. Several ring-substituted derivatives of styrene and 1-phenyl-1,3-butadiene were prepared according to the known methods¹⁷ with or without a slight modification. Other starting substrates in this research were commercial products. Except for (phthalocyanine)cobalt and $\text{Co}(\text{TPP})$, which are commercially available, $\text{Co}(\text{DH})_2(\text{py})\text{Cl}$, $\text{Co}(\text{DH})_2(\text{H}_2\text{O})_2$, $\text{Co}(\text{salen})$ [H_2salen = 2,2'-ethylenebis(nitrilo-methylidene)diphenol], and $\text{Co}(\text{sacac})_2(\text{en})$ [$\text{H}_2(\text{sacac})_2(\text{en})$ =

ethylenebis(nitrilo-2-pentylidene-4-thione)] were synthesized by the procedure in the literature.¹⁸ The organometallic compound $\text{CH}_3\text{CH}(\text{Ph})\text{Co}(\text{DH})_2(\text{py})$ was also synthesized according to the known method¹⁹ and stored in a cold and dark place. The organic solvents used for nitrosation was deaerated before use. Other chemicals than those above-mentioned were purchased and used without further purification. Product analyses by gas chromatography were carried out on a Shimadzu 4BM-PF apparatus, using EGSS-X (3% or 15%)-Chromosorb-W (100 \times 0.3 cm or 300 \times 0.3 cm) and Silicone OV-1 (2%)-Shimalite (100 \times 0.3 cm) columns with nitrogen as carrier gas.

Catalytic Nitrosation of Aryl-Substituted Olefins in the Presence of BH_4^- (Table I and Entries 1-10 in Table II). The catalytic reaction was carried out with 12.2 mmol of each substrate by the general procedure described below. In a three-neck flask were placed successively a catalyst and a reducing agent (TEA or TBA) in the amounts indicated in Tables I and II. The system was evacuated and then filled with an atmospheric pressure of NO by connecting the system with a NO-containing vessel. To the system were added successively 2.5 mL each of isopropyl alcohol and 1,2-dimethoxyethane and a further 12.2 mmol of starting substrate. After being stirred for an appropriate time at room temperature, the system was treated with 10 mL of water plus 30 mL of ether under stirring. The ether layer was separated and the aqueous layer was extracted with two 30-mL portions of ether. The combined organic layers were dried over Na_2SO_4 and distilled under reduced pressure to afford a residue, which was subjected to column chromatography on silica gel using ethyl acetate-hexane (1:5 volume ratio) as an eluent.

Stoichiometric Nitrosation of $\text{CH}_3\text{CH}(\text{Ph})\text{Co}(\text{DH})_2(\text{py})$ with or without BH_4^- (Entries 11 and 12 in Table II). In a flask were placed 0.20 mmol of the complex and 0.20 mmol of TEA when necessary. The system was then evacuated and filled with NO by the same method as above. To the system was added successively 1.5 mL each of isopropyl alcohol and 1,2-dimethoxyethane. After being stirred for 5 h at room temperature, the mixture was treated with 5 mL of water plus 15 mL of ether under stirring. The ether layer was separated, and the aqueous layer was extracted with two 15-mL portions of ether. The combined organic layers were dried over Na_2SO_4 and concentrated to an appropriate volume under reduced pressure in order to submit to the analysis by gas chromatography.

Registry No. $\text{PhCH}=\text{CH}_2$, 100-42-5; *o*- $\text{ClC}_6\text{H}_4\text{CH}=\text{CH}_2$, 2039-87-4; *p*- $\text{ClC}_6\text{H}_4\text{CH}=\text{CH}_2$, 1073-67-2; *o*- $\text{BrC}_6\text{H}_4\text{CH}=\text{CH}_2$, 2039-88-5; *o*- $\text{CH}_3\text{C}_6\text{H}_4\text{CH}=\text{CH}_2$, 611-15-4; *p*- $\text{CH}_3\text{C}_6\text{H}_4\text{CH}=\text{CH}_2$, 622-97-9; *m*- $\text{O}_2\text{NC}_6\text{H}_4\text{CH}=\text{CH}_2$, 586-39-0; *p*- $\text{CH}_3\text{OC}_6\text{H}_4\text{CH}=\text{CH}_2$, 637-69-4; *o*- $\text{CH}_2=\text{CHC}_6\text{H}_4\text{CH}=\text{CH}_2$, 91-14-5; *o*- $\text{CH}_2=\text{CHCH}_2\text{OC}_6\text{H}_4\text{CH}=\text{CH}_2$, 21919-44-8; $\text{PhCH}=\text{CHCH}=\text{CH}_2$, 1515-78-2; $\text{PhCH}=\text{CHCH}_2\text{OH}$, 104-54-1; $\text{PhC}\equiv\text{CH}$, 536-74-3; $\text{PhCH}(\text{Br})\text{CH}_3$, 585-71-7; $\text{PhCH}=\text{CHCH}_2\text{Br}$, 4392-24-9; $\text{PhC}(\text{CH}_3)=\text{NOH}$, 613-91-2; *o*- $\text{ClC}_6\text{H}_4\text{C}(\text{CH}_3)=\text{NOH}$, 7147-44-6; *p*- $\text{ClC}_6\text{H}_4\text{C}(\text{CH}_3)=\text{NOH}$, 1956-39-4; *o*- $\text{BrC}_6\text{H}_4\text{C}(\text{CH}_3)=\text{NOH}$, 27760-49-2; *o*- $\text{CH}_3\text{C}_6\text{H}_4\text{C}(\text{CH}_3)=\text{NOH}$, 27810-08-8; *p*- $\text{CH}_3\text{C}_6\text{H}_4\text{C}(\text{CH}_3)=\text{NOH}$, 2089-33-0; *m*- $\text{O}_2\text{NC}_6\text{H}_4\text{C}(\text{CH}_3)=\text{NOH}$, 7471-32-1; *p*- $\text{CH}_3\text{OC}_6\text{H}_4\text{C}(\text{CH}_3)=\text{NOH}$, 2475-92-5; *o*- $\text{CH}_2=\text{CHC}_6\text{H}_4\text{C}(\text{CH}_3)=\text{NOH}$, 110372-51-5; *o*- $\text{CH}_2=\text{CHCH}_2\text{OC}_6\text{H}_4\text{C}(\text{CH}_3)=\text{NOH}$, 110372-52-6; $\text{PhCH}=\text{CHC}(\text{CH}_3)=\text{NOH}$, 2887-98-1; $\text{PhC}(\text{NOH})\text{CH}_2\text{CH}_2\text{OH}$, 110372-53-7; $\text{PhCH}=\text{CHCH}=\text{NOH}$, 13372-81-1; $\text{CH}_3\text{CH}(\text{Ph})\text{Co}(\text{DH})_2(\text{py})$, 37824-58-1; $\text{Co}(\text{DH})_2(\text{py})(\text{NO}_2)$, 42741-17-3; $\text{CH}_2=\text{C}(\text{Ph})\text{Co}(\text{DH})_2(\text{py})$, 56498-38-5; acenaphthalene, 208-96-8; 1(2*H*)-acenaphthylene oxime, 5088-53-9.

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(15) $\text{CH}_2=\text{C}(\text{Ph})\text{Co}(\text{DH})_2(\text{py})$: IR (KBr) 3450, 1600, 1560, 1558, 1480, 1445, 1240, 1090, 890 cm^{-1} . Anal. Calcd for $\text{C}_{21}\text{H}_{26}\text{CoN}_5\text{O}_4$: C, 53.51; H, 5.56; N, 14.86. Found: C, 52.94; H, 5.61; N, 14.58. $\text{Co}(\text{DH})_2(\text{py})(\text{NO}_2)$: IR (KBr) 1420, 1315, 1275, 820 cm^{-1} . Anal. Calcd for $\text{C}_{13}\text{H}_{19}\text{CoN}_5\text{O}_6$: C, 37.69; H, 4.62; N, 20.29. Found: C, 37.25; H, 4.75; N, 19.60.

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