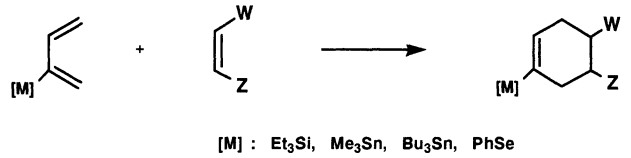
Diels-Alder Reaction of (1-Methylene-2-propenyl)cobaloxime, 1-Methylene-2-propenyl-bis(dimethylglyoximato)pyridine-cobalt(III)

Masaru TADA* and Tamaki SHIMIZU
Department of Chemistry, School of Science and Engineering,
Waseda University, Shinjuku, Tokyo 169
(Received November 19, 1991)

(1-Methylene-2-propenyl)cobaloxime (**1**), a diene having a transition metal substituent, was prepared conveniently from 2-chloromagnesio-1,3-butadiene and chlorocobaloxime. Cobaloxime **1** gives Diels–Alder adducts with olefinic dienophiles (maleic anhydride, *N*-phenylmaleimide, *p*-benzoquinone, dimethyl fumarate, methyl vinyl ketone, and methyl acrylate) and acetylenic dienophiles (methyl propiolate and dimethyl acetylenedicarboxylate). The reactivity of cobaloxime **1** is higher than that of its metalloid analogs, such as 2-silyl-, 2-seleno-, and 2-stannyl-1,3-butadiene, though the reaction pattern is essentially the same. This additional activation of the diene system by cobaloxime is accounted for by a back donation of the filled d-orbital of cobalt(III) to the π-system of the diene.

The Diels–Alder addition is one of the most versatile and useful reactions in the construction of six-membered ring systems.[1-4] Modification of butadiene by metal substitution has been tried by Bates and Ganen's groups for improving the reactivity. Bates et al. used 2-trialkylstannyl-1,3-butadiene and 2-phenylseleno-1,3-butadiene,[5] and Batt and Ganen used 2-trialkylsilyl-1,3-butadiene as diene[6] [Scheme 1]. These heteroatoms are all typical elements; the effect of the metal substituents is transmitted through the metal–carbon σ-bond and conjugation between π(diene) and vacant d-orbital of the heteroatom.

In this paper we report on the Diels–Alder reaction of 1-methylene-2-propenyl-bis(dimethylglyoximato)pyridinecobalt(III) (**1**) (Fig. 1), (1-methylene-2-propenyl)cobaloxime hereafter, with a variety of dienophiles. The bond between cobalt and butadiene is based on the coordination of sp^2(butadiene)–d_{z^2}(cobalt) and is considered to be reinforced by a backdonation of the filled $d_{xz,yz}$(cobalt) to π*(butadiene), as illustrated by the dπ–dπ interaction in a cobalt–sulfur bond.[7] This type of backdonative interaction can not be expected for silyl, stannyl, and selenobutadiene; these aspects of the cobalt–diene bond prompted us to investigate the Diels–Alder reaction of the readily available (1-methylene-2-propenyl)cobaloxime (**1**).



Scheme 1.

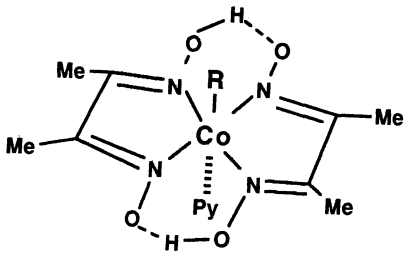
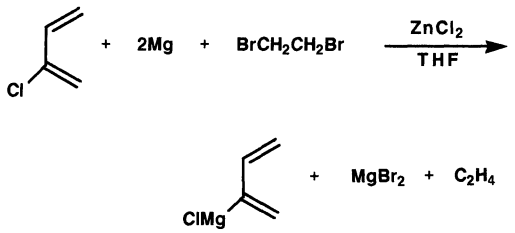


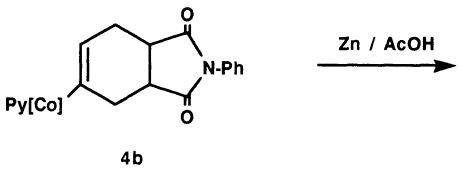
Fig. 1. Chlorocobaloxime and (1-methylene-2-propenyl)cobaloxime (**1**).

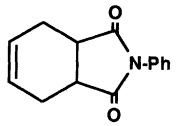
Results and Discussion

The starting material (1-methylene-2-propenyl)cobaloxime (**1**) was prepared by reacting chlorocobaloxime(III) (Fig. 1. R=Cl) with 2-chloromagnesio-1,3-butadiene. Chloro-cobaloxime[8] was easily prepared from its components by an open-aired one-pot reaction and 2-chloromagnesiobutadiene was prepared in situ from 2-chlorobutadiene by the process shown in Eq. 1.[9]



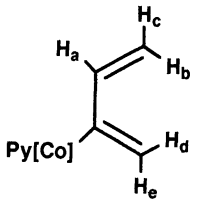
(1)





(2)

The structure of cobaloxime **1** was unequivocally proved by its 400 MHz ^{1}H NMR spectrum (Fig. 2).

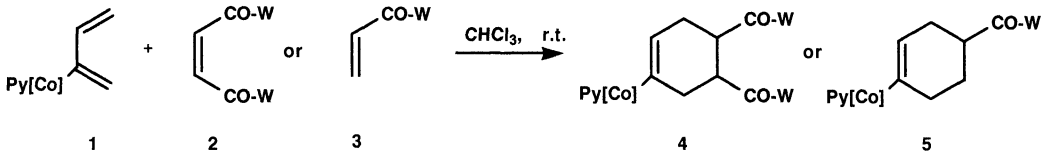


δ=6.47 (a), 4.83 (b), 4.59 (c), 4.54 (d), 4.44 (e)
J_{ab}=16.7 Hz, J_{ac}=10.3 Hz
J_{ae}=1.6 Hz, J_{bc}=2.8 Hz

Fig. 2. ^{1}H NMR spectrum of (1-methylene-2-propenyl)cobaloxime (**1**).

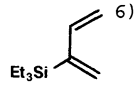
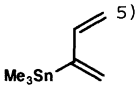
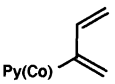
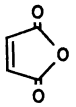
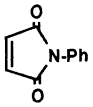
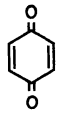
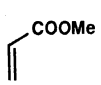
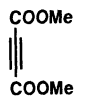
An equimolar mixture of (1-methylene-2-propenyl) cobaloxime (**1**) and one of the dienophiles in chloroform was reacted in the dark. The reaction was monitored by TLC analyses on silica gel; it was stopped upon disappearance of the starting dienophile. The reaction conditions and yields are shown in the fourth column of Table 1.

The structures of products **4a**, **4b**, and **4c** (Fig. 3) from maleic anhydride, *N*-phenylmaleimide, and *p*-benzoquinone, respectively were unambiguously assigned from ^{1}H NMR spectral data (400 MHz) on the basis of the chemical shifts, coupling constants, and ^{1}H–^{1}H two-



Scheme 2.

Table 1. Reaction Conditions (Solvent, Reaction Temperature (°C)/Reaction Time (h)) and Yields of the Diels–Alder Reaction of 2-Metal-Substituted 1,3-Butadienes

Dienophile	Diene		
	 6)	 5)	 (This work)
	Neat r.t./3 75%	Toluene r.t./48 75%	Chloroform r.t./2.5 80% (**4a**)
	Neat 100/3 80%	Toluene 110/8 90%	Chloroform r.t./24 88% (**4b**)
	Neat 110/3 67%	Toluene 110/8 69%	Chloroform r.t./45 90% (**4c**)
	Benzene–chloroform (1:1), reflux/10 81%	Neat 100/8 69%	Chloroform r.t./45 92% (**4d**)
	—	Benzene 80/12 50% (3:1)	Chloroform r.t./24 (**5a**) 92%
	Benzene 80/6 77% (3.3:1)	Toluene 110/18 72% (2:1)	Benzene 80/5 87% (4:1) (**5b**, **b′**)
	—	—	Benzene r.t./68 94% (**6**)
	Benzene 80/10 87%	Toluene 110/18 71%	Chloroform r.t./48 84% (**7**)

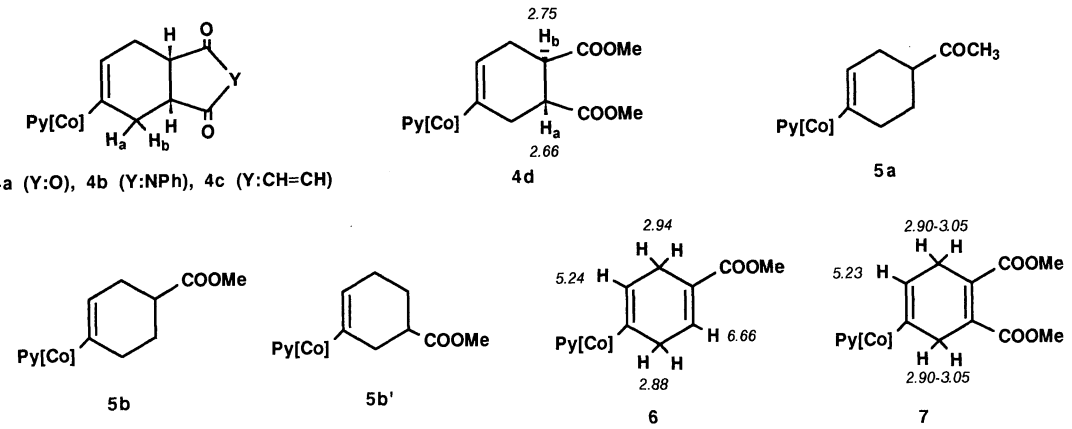


Fig. 3. Structures and ^{1}H NMR chemical shifts of the Diels–Alder adducts of (1-methylene-2-propenyl)cobaloxime (**1**).

dimensional spectra. A common feature of these spectra was found in signals due to the methylene protons (H_a and H_b) next to the cobaloxime moiety. The chemical shifts of those protons are largely separated (δ=0.49—0.96) due to anisotropic shielding by the carbonyl and cobaloxime groups. One of them resonates at δ=1.94 (**4a**), 2.00 (**4b**), and 2.07 (**4c**); another resonates at δ=2.90 (**4a**), 2.87 (**4b**), and 2.56 (**4c**). These methylene protons couple with each other with a large coupling constant of 16—17 Hz, but show very small coupling, if any, with the adjacent methine proton. Product **4b** was further correlated with the adduct between butadiene and *N*-phenylmaleimide.[10] The cobaloxime moiety in the adduct **4b** was removed by reduction with zinc–acetic acid (Eq. 2).

Structure **4d** (Fig. 3) for the adduct from dimethyl fumarate was assigned on the basis of the following ^{1}H NMR spectral analyses. ^{1}H–^{1}H two-dimensional spectrum and chemical shifts show unequivocally that the methine protons (H_a and H_b (δ=2.66 and 2.75 or vice versa)) couple with the three adjacent protons (H_a, J=11.0, 11.0, and 5.1 Hz; H_b, J=11.0, 11.0, and 5.5 Hz). These spectral features, two sets of vicinal diaxial coupling and one set of vicinal axial-equatorial coupling, show that H_a and H_b are in trans relation. This stereochemistry suggests a general concerted mechanism for this reaction.

The structures of adducts **5a, 5b,** and **5b′**, and therefore the regiochemistry of the reaction, remain ambiguous, even after ^{1}H–^{1}H two-dimensional and decoupling experiments. Bates et al. reported that a nuclear Overhauser measurement (400 MHz) with a similar system having a trialkylstannyl substituent other than cobaloxime gave no clear discrimination.[5] Structures **5a, 5b,** and **5b′**, therefore, were tentatively assigned by analogy to reactions of the same dienophile with the butadiene derivatives having metal substituents[5,6] as well as on the basis of both theoretical[11] and experimental studies already reported.[12] Thus, the addition reaction can be illustrated by a general scheme 2.

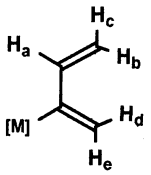
Acetylenic esters are less reactive than the olefinic counterparts but they are still good dienophiles to give adducts under mild conditions and in high yields (Table 1). Adduct **6** (Fig. 3) has ^{1}H NMR signals due to two olefinic protons (δ=5.24 and 6.66) and four protons of methylene groups (δ=2.88 and 2.94). Irradiation of the olefinic proton at δ=6.66 (β-position to the ester) modified only the methylene signals at δ=2.88, while irradiation at δ=5.24 modified only the methylene signals at δ=2.94. These observations clearly prove the structure **6** as well as the complete regiospecificity of the addition reaction.

Structure **7** for the adduct from dimethyl acetylenedicarboxylate is evident from the ^{1}H NMR signals: A multiplet 2.90—3.05 ppm for the four methylene protons and a multiplet at 5.20—5.25 ppm for one olefinic proton.

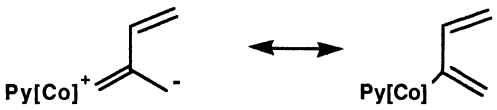
The reaction pattern of (1-methylene-2-propenyl)cobaloxime (**1**) with a variety of dienophiles is essentially the same as those of the butadiene derivatives having a metal substituent at the 2-position, 2-trialkylsilyl and 2-trialkylstannyl.[5,6] The reactivity and regioselectivity of cobaloxime **1**, however, is much higher, as shown in Table 1. 2-Trialkylsilyl- and 2-trialkylstannyl-1,3-butadiene gave similar adducts in 67—90% yields, mostly at 80—110°C.[5,6] (1-Methylene-2-propenyl)cobaloxime (**1**) gave adducts with these dienophiles in higher yields (80—92%) at room temperature.

Though the reaction conditions and yields listed in Table 1 allow us only a qualitative discussion, the reaction conditions in our present study were milder, and the yields better than those of the silyl and stannyl derivatives. These results show that the butadiene system is more activated by cobaloxime than by the silyl or stannyl substituent. This additional activation must be due to the electron-donating character of the cobalt(III) by $d\pi$–$p\pi$ delocalozation, depicted by the resonance expression in Scheme 3. This feature is in

Table 2. ^{1}H NMR Chemical Shifts (ppm) of 2-Metal-substituted 1,3-Butadiene



[M]	Ha	Hb	Hc	Hd,e
Et_3Si[6]	6.45	5.23	4.98	(5.39, 5.82)
Me_3Sn[5]	6.5	4.9	5.0	(5.3, 5.8)
Py[Co]	6.47	4.83	4.59	(4.44, 4.54)
Me[14]	6.55	5.00—5.40		5.06



Scheme 3.

accord with the chemical shifts of 2-metal-substituted 1,3-butadienes (Table 2). Though the chemical shifts of H_a remain within a small range, those of H_d and H_e are greatly affected by metal substituents. In comparison with 2-methyl-1,3-butadiene, the cobaloxime substituent markedly shifts the H_d and H_e signals to a higher magnetic field, whereas the other metal substituents shift them to a lower field. Protons H_b and H_c are also affected by the metal substituents, especially by cobaloxime. We understand these features to be a reflection of the difference in the interactions between metal and diene. Silyl and stannyl substituents transmit their effect mainly through the σ-bond, whereas the cobaloxime affects through a $p\pi$–$d\pi$ interaction.

In conclusion, (1-methylene-2-propenyl)cobaloxime behaves as an activated diene in Diels–Alder reactions with dienophiles having an electron-withdrawing group. The activation is more remarkable than in the case of butadienes with a silyl, seleno, or stannyl substituent. The activation can be accounted for in terms of the back-donative interaction by $d\pi$(cobalt)–$p\pi$(butadiene) delocalization.

Experimental

The dienophiles used in this study were obtained from Tokyo Kasei Co. or Aldrich Chemical Co., and were used without purification. 2-Chlorobutadiene was provided by Denki Kagaku Industry Co. as a benzene solution, and were used as the solution. The IR spectra were recorded on a Perkin-Elmer 1640 FT-IR spectrometer or a Shimadzu IR-400 spectrometer in a chloroform solution. The ^{1}H NMR spectra were measured by JEOL GSX-400 spectrometer (400 MHz) in deuteriochloroform. Chemical shifts and coupling constants are recorded in ppm with TMS used as the standard and Hz, respectively. Elemental analyses were carried out at the analytical center of the Science and Engineering Institute of Waseda University.

Synthesis of (1-Methylene-2-propenyl)cobaloxime (1). i) 2-Chloromagnesio-1,3-butadiene:[9] A mixture of magnesium (4.0 g, 0.17 mol), 1,2-dibromoethane (1.0 mL), and 2 mL of THF was heated to reflux under nitrogen for 30 min to activate magnesium. To the mixture was added anhydrous zinc chloride (0.6 g) in 50 mL of THF; then, 2-chlorobutadiene (9.2 mL, 0.1 mol) and 1,2-dibromoethane (3.8 g, 0.02 mol) in 50 mL of THF were added dropwise over a period of 40 min. This addition was controlled so as to bring the mixture into a gentle exothermic reaction with the evolution of gas; the mixture was heated to reflux for 30 min after completing the addition. The Grignard reagent, thus obtained, was used immediately for the synthesis of (1-methylene-2-propenyl)cobaloxime.

ii) (1-Methylene-2-propenyl)cobaloxime (1): The Grignard reagent obtained as mentioned above was quickly transferred to a dropping funnel and added dropwise to chloro-bis(dimethylglyoximato)pyridinecobalt(III)[8] (12.9 g, 0.32 mol) in 80 mL of THF, for 15 min under cooling in an ice-bath. The reaction mixture was stirred for an additional 10 min at ambient temperature; then, ice-water (320 mL), chloroform (200 mL), and concentrated hydrochloric acid (7 mL) were added. The organic layer was washed with saturated sodium hydrogencarbonate and water, and dried over sodium sulfate. The residue after evaporation of the solvent was passed through a short column of Florisil (4.5×10.0 cm) using ethyl acetate in order to remove any polar materials. The yellow crystalline material, thus obtained, was purified by recrystallization from ethanol to give (1-methylene-2-propenyl)cobaloxime (**1**) in 44% yield.

1: Mp 203.5—207.0°C (decomp); IR 1600, 1558, 1444, 1090 cm^{-1}; ^{1}H NMR δ=2.12 (12H, s), 4.44 (1H, d, J=1.6), 4.54 (1H, s), 4.59 (1H, dd, J=10.3 and 2.8), 4.83 (1H, dd, J=16.7 and 2.8), 6.47 (1H, ddd, J=16.7, 10.3, and 1.6), 7.30—7.37 (2H, m), 7.72 (1H, tt, J=7.7 and 1.5), 8.64 (2H, dd, J=6.4 and 1.5), 18.25 (2H, br. s). See Fig. 2 for the assignment. Found: C, 48.39; H, 5.78; N, 16.51%. Calcd for $C_{17}H_{24}N_5O_4Co$: C, 48.47; H, 5.74; N, 16.62%.

General Procedure of Diels-Alder Addition. (1-Methylene-2-propenyl)cobaloxime (**1**) (211 mg, 0.50 mmol) and one of the dienophiles (0.50 mmol) in 1.0 mL of chloroform were stirred magnetically in the dark at ambient temperature. After disappearance of the dienophile on TLC analysis, the solvent was evaporated and the residue passed through a short column of Florisil (1.5×3.0 cm) using first chloroform and then ethyl acetate to collect the yellow band. This procedure gave essentially pure adducts and further purified by recrystallization from methanol (**4a**) or acetonitrile (other than **4a**).

Adduct 4a from Maleic Anhydride. Mp 220.0—222.5°C (decomp); IR 1842, 1779, 1605, 1563, 1452, 1094 cm^{-1}; ^{1}H NMR δ=1.94 (1H, d, J=16.1), 2.10 (6H, s), 2.11 (6H, s), 2.14—2.22 (1H, m), 2.60 (1H, ddd, J=14.7, 7.3, and 1.8), 2.90 (1H, d, J=16.1), 3.14—3.24 (2H, m), 5.66—5.69 (1H, m), 7.29—7.33 (2H, m), 7.72 (1H, tt, J=7.7 and 1.5), 8.60 (2H, dd, J=6.6 and 1.5), 18.14 (2H, br. s). Found: C, 48.27; H, 5.12; N, 13.38%. Calcd for $C_{21}H_{26}N_5O_7Co$: C, 48.56; H, 5.05; N, 13.48%.

Adduct 4b from *N*-Phenylmaleimide. Mp 233.5—235.0°C (decomp); IR 1702, 1563, 1380, 1091 cm^{-1}; ^{1}H NMR δ=1.90 (6H, s), 1.95 (6H, s), 2.00 (1H, d, J=16.1), 2.28—2.37 (1H, m), 2.67 (1H, ddd, J=14.7, 7.3, and 1.5), 2.87 (1H, dd, J=16.1 and

2.2), 2.98—3.10 (2H, m), 5.44—5.50 (1H, m), 7.24—7.45 (7H, m), 7.68 (1H, tt, J=7.7 and 1.5), 8.57 (2H, dd, J=6.2 and 1.5), 18.16 (2H, br. s). Found: C, 54.59; H, 5.36; N, 14.14%. Calcd for $C_{27}H_{31}N_6O_6Co$: C, 54.55; H, 5.26; N, 14.14%.

Adduct 4c from *p*-Benzoquinone. Mp 243.0—245.0°C (decomp); IR 1693, 1604, 1566, 1458, 1087 cm^{-1}; ^{1}H NMR δ=2.07 (1H, d, J=17.2), 2.12 (6H, s), 2.15 (6H, s), 2.20—2.29 (1H, m), 2.37—2.47 (1H, m), 2.56 (1H, d, J=17.2), 3.02—3.12 (2H, m), 5.13—5.17 (1H, m), 6.50 (1H, d, J=10.3), 6.54 (1H, d, J=10.3), 7.28—7.34 (2H, m), 7.71 (1H, tt, J=7.7 and 1.5), 8.63 (2H, dd, J=6.2 and 1.5), 18.15 (2H, br. s). Found: C, 51.98; H, 5.43; N, 13.30%. Calcd for $C_{23}H_{28}N_5O_6Co$: C, 52.18; H, 5.33; N, 13.23%.

Adduct 4d from Dimethyl Fumarate. Mp 227.0—230.5°C (decomp); IR 1730, 1604, 1563, 1442, 1170, 1085 cm^{-1}; ^{1}H NMR δ=1.91—2.01 (1H, m), 2.10 (6H, s), 2.11 (6H, s), 2.15—2.25 (1H, m), 2.40 (1H, dddd, J=17.4, 5.5, 5.5, and 1.5), 2.51 (1H, dd, J=17.4 and 5.1), 2.66 (1H, ddd, J=11.0, 11.0, and 5.1), 2.75 (1H, ddd, J=11.0, 11.0, and 5.1), 3.62 (3H, s), 3.67 (3H, s), 5.13—5.19 (1H, m), 7.28—7.37 (2H, m), 7.71 (1H, tt, J=7.7 and 1.5), 8.60 (2H, dd, J=6.6 and 1.5), 18.13 (2H, br. s). Found: C, 48.65; H, 5.70; N, 12.62%. Calcd for $C_{23}H_{32}N_5O_8Co$: C, 48.85: H, 5.70; N, 12.39%.

Adduct 5a from Methyl Vinyl Ketone. Mp 215.0—220.0°C (decomp); IR 1700, 1608, 1565, 1453, 1084 cm^{-1}; ^{1}H NMR δ=1.54 (1H, dddd, J=22.0, 11.0, 5.0, and 1.8), 1.68—1.79 (1H, m), 1.87—2.00 (1H, m), 2.07 (3H, s), 2.10 (12H, s), 2.18—2.29 (3H, m), 2.37—2.47 (1H, m), 5.08—5.15 (1H, m), 7.28—7.37 (2H, m), 7.70 (1H, tt, J=7.7 and 1.5), 8.62 (2H, dd, J=6.4 and 1.5), 18.15 (2H, br. s). Found: C, 51.29; H, 6.10; N, 14.34%. Calcd for $C_{21}H_{30}N_5O_5Co$: C, 51.33; H, 6.15; N, 14.25%.

Adduct 5b and 5b′ from Methyl Acrylate. The same procedure as with other dienophiles afforded a 4.5 : 1 mixture (4 : 1 at 80°C) of **5b** and **5b′**. Although most of the ^{1}H NMR signals of the two isomers overlap with each other, the methyls of the ester groups showed different chemical shifts (δ=3.62 for **5b** and 3.63 for **5b′**). The mixture could not be separated by chromatography, and the product ratio was determined by the relative intensities of these signals. (**5b** and **5b′**, 4.5:1 mixture); IR 1718, 1605, 1560, 1451, 1080 cm^{-1}; ^{1}H NMR δ=1.66 (1H, ddt, J=22.7, 5.5, and 5.5), 1.75—1.83 (1H, m), 1.87—2.00 (1H, m), 2.10 (12H, s), 2.17–2.32 (3H, m), 2.33—2.43 and 2.44—2.52 (total 1H, m), 3.62 and 3.63 (total 3H, s), 5.06—5.14 (1H, m), 7.27—7.38 (2H, m), 7.70 (1H, tt, J=7.7 and 1.5), 8.65 (2H, dd, J=6.4 and 1.5), 18.15 (2H, br. s). Found: C, 49.64: H, 5.98; N, 13.89%. Calcd for $C_{21}H_{30}N_5O_6Co$: C, 49.71; H, 5.96; N, 13.80%.

Adduct 6 from Methyl Propiolate. Mp 216.0—228.0°C (decomp); IR 1706, 1664, 1605, 1555, 1451, 1250, 1063 cm^{-1}; ^{1}H NMR 2.10 (12H, s), 2.88 (2H, m), 2.94 (2H, m), 3.68 (3H, s), 5.24 (1H, t, J=1.0), 6.66 (1H, t, J=1.0), 7.28—7.33 (2H, m), 7.72 (1H, tt, J=7.7 and 1.5), 8.63 (2H, dd, J=6.4 and 1.5), 18.15 (2H, br. s). Found: C, 49.90; H, 5.59; N, 13.95%. Calcd for $C_{21}H_{28}N_5O_6Co$: C, 49.91; H, 5.58; N, 13.86%.

Adduct 7 from Dimethyl Acetylenedicarboxylate. Mp 230.0—231.5°C (decomp); IR: 1715, 1657, 1604, 1555, 1451, 1250, 1063 cm^{-1}; ^{1}H NMR δ=2.10 (12H, s), 2.90—3.05 (4H, m), 3.71 (3H, s), 3.77 (3H, s), 5.20—5.25 (1H, m), 7.28—7.38 (2H, m), 7.72 (1H, tt, J=7.7 and 1.5), 8.69 (2H, dd, J=6.4 and 1.5), 18.19 (2H, br. s). Found: C, 49.11; H, 5.34; N, 12.61%. Calcd for $C_{23}H_{30}N_5O_8Co$: C, 49.03; H, 5.37; N, 12.43%.

The Reduction of *N*-Phenylmaleimide Adduct (4b) by Zinc-Acetic Acid. A mixture of adduct **4b** (242 mg, 0.40 mmol), activated zinc powder (400 mg, 6.0 mmol), 30 mL of methanol, and 10 mL of 10% aqueous acetic acid was stirred for 18 h at room temperature. The reaction mixture was filtered and saturated aqueous sodium chloride added to the filtrate; the mixture was then extracted with chloroform. The extracts were dried over sodium sulfate and passed through a short column of silica gel (1.0×12.0 cm). The chloroform eluate gave the adduct of butadiene with *N*-phenylmaleimide;[10] IR 1708, 1500, 1386, 1173 cm^{-1}; ^{1}H NMR δ=2.40(2H, d, J=15.0), 2.76 (2H, d, J=15.0), 3.20—3.45 (2H, m), 5.96—6.30 (2H, m), 7.06—7.80 (5H, m).

This work was supported by the fund from the Asahi Glass Foundation. The authors are indebted to Denki Kagaku Industry Co. for the generous supply of 2-chlorobutadiene.

References

1) a) M. C. Klotzel, "Organic Reactions," ed by R. Adams, John-Wiley and Sons, New York (1948), Vol. 4, p. l; b) H. L. Holmes, *ibid.*, (1949), Vol. 5, p. 61; c) L. W. Butz and A. W. Rytina, *ibid.*, (1949), Vol. 5, p. 136.

2) R. Huisgen, R. Grashey, and J. Sauer, "The Chemistry of Alkenes," ed by S. Patai, Wiley-Interscience, New York (1964), p. 878.

3) J. Sauer, *Angew. Chem., Int. Ed. Engl.*, **5**, 211 (1966).

4) S. M. Weinreb and R. R. Staib, *Tetrahedron*, **38**, 3087 (1982).

5) G. S. Bates, M. P. Fryzuk, and S. Stone, *Can. J. Chem.*, **65**, 2612 (1987).

6) D. G. Batt and B. Ganen, *Tetrahedron Lett.*, **1978**, 3323.

7) M. Tada and R. Shino, *J. Inorg. Biochem.*, **44**, 89 (1991).

8) G. N. Schrauzer, "Inorganic Syntheses," McGraw-Hill, New York (1968), Vol. XI, p. 62.

9) S. Nunomoto and Y. Yamashita, *J. Org. Chem.*, **44**, 4788 (1979).

10) E. Schefczik, *Chem. Ber.*, **98**, 1270 (1965).

11) C. L. Liotta and J. W. Verbicky, *Tetrahedron Lett.*, **1985**, 1395.

12) O. Eisenstein, J. M. Lefour, and N. T. Anh, *Tetrahedron*, **33**, 523 (1977).

13) K. G. Allum, R. D. Hancock, I. V. Howell, R. C. Pitkethly, and P. J. Robinson, *J. Organomet. Chem.*, **87**, 189 (1975).

14) C. J. Pouchert and J. R. Campbel, "The Aldrich Library of NMR Spectra," Vol. I, 29c, Aldrich, Milwaukee (1974).