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Preparation of transition metal isoxazole derivatives

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Abstract

η^1-Ethynyl complexes $\mathrm{Cp(CO)_nLMC{\equiv}CPh}$ ($n = 1, 2$; $\mathrm{L = CO, PPh_3}$; $\mathrm{M = Fe, Mo}$) react with nitrile oxides $\mathrm{RC{\equiv}N{\rightarrow}O}$ ($\mathrm{R = Ph, CO_2Et}$) to give the σ-isoxazolyl transition metal derivatives $\mathrm{Cp(CO)_nLM{-}\overline{C{=}C(Ph)C(R){=}N{-}O}}$, which have been characterized by IR and ^{1}H NMR spectroscopy. An X-ray diffraction study of $\mathrm{Cp(OC)(Ph_3P)Fe{-}\overline{C{=}C(Ph)C(Ph){=}N{-}O}}$ is described.

Introduction

Transition metal heterocyclic derivatives are of considerable interest for studies on biological activity [1]. Heterocycles can coordinate transition metal atoms in various ways, viz. (i) π-coordination (η^5- or η^6-heterocyclic ligands analogous to cyclopentadienyl or π-arene) [2–4], (ii) formation of n-donor complexes because of donation of the heteroatom lone electron pair to the metal atom (this is most common for nitrogen-containing heterocycles) [5,6] and, (iii) formation of a σ-bond by the transition metal atom with the carbon or the heteroatom of the heterocycle [5–8]. The latter class of the complexes is prepared by reactions of metallated heterocycles and compounds with activated halogen atoms [9], by oxidative addition of heterocycles with halogen-carbon bonds to low-valent metal complexes [10,11], and by cycloaddition of activated multiple bonds to complexes with unsaturated σ ligands [7,8,12]. We recently reported the preparation of pyrazoles with Fe–C σ bonds by the reaction of (π-cyclopentadienyl)dicarbonyl(σ-sydnonyl)iron with acetylenedicarboxylates, in which the sydnone acts as a 1,3-dipolar azomethynimine [13].

Here we describe the novel preparation of isoxazoles, containing a metal carbonyl substituent in the 5 position, by 1,3-dipolar cycloaddition of nitrile oxides to transition metal σ-alkynyls.

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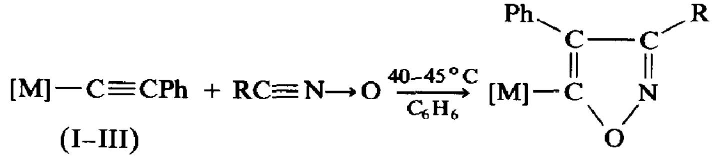
Results and discussion

The reactions of 1,3-dipolar cycloaddition are a well-known and effective synthetic route to various heterocycles [14]. However, such addition to transition metal complexes with unsaturated σ-ligands has not been studied previously.

We have found (see also ref. 15) that (η^5-cyclopentadienyl)(η^1-phenylethynyl)dicarbonyliron (I), (η^5-cyclopentadienyl)(η^1-phenylethynyl)(triphenylphosphine)carbonyliron (II), and (η^5-cyclopentadienyl)(η^1-phenylethynyl)(triphenylphosphine)dicarbonylmolybdenum (III) react with benzonitrile oxide or carboethoxynitrile oxide, generated in situ from the corresponding hydroxamic acid chlorides, PhC(Cl)=N–OH (IV) or EtOOCC(Cl)=N–OH (V), to give the σ-isoxazol-5-yl complexes (VI–X):



(I–III)

(VI–X)

$[M] = (\eta^5\text{-}C_5H_5)(CO)_2Fe$, R = Ph (VI); R = CO_2Et (VII)
$[M] = (\eta^5\text{-}C_5H_5)(CO)(PPh_3)Fe$, R = Ph (VIII); R = CO_2Et (IX)
$[M] = (\eta^5\text{-}C_5H_5)(CO)_2(PPh_3)Mo$, R = Ph (X)

This 1,3-dipolar addition proceeds by an electron density redistribution in the alkynyl ligand [16]. Partial negative and positive charges on the β- and α-carbon atoms, respectively, in the complexes I–III determine the formation of isoxazoles with a metal carbonyl residue in the 5 position.

The complexes VI–X are crystalline, air-stable compounds, which decompose slowly in solution. Their structure has been confirmed by IR and ^1H NMR spectroscopic data (Table 1) and by an X-ray diffraction study of VIII.

Thus, in the IR spectrum of VI the CO groups stretching frequencies (2040 and 2000 cm^{-1}) show almost no shift as compared with the parent acetylenide I (2035 and 1995 cm^{-1}), being only slightly affected by the benzonitrile oxide cycloaddition. However, the cycloaddition of carboethoxynitrile oxide results in the shift of one ν(C≡O) band by 15 cm^{-1} to lower frequencies (see Table 1). In contrast, cycloaddition of 1,3-dipoles to the phosphine-substituted acetylenide II increases ν(C≡O) by 15–20 cm^{-1} compared with 1925 cm^{-1} in the spectrum of the parent compound II, but the type of substituent (Ph or CO_2Et) does not affect the CO stretching frequencies of VIII and IX (see Table 1). In the IR spectrum of X the CO bands (1960 and 1880 cm^{-1}) almost coincide with those of the parent acetylenide III. The spectra of VII and IX contain besides the ν(C≡O), bands, the stretching frequency bands at 1730 and 1740 cm^{-1} of the ester group C=O bond.

The structure of VIII was confirmed by an X-ray diffraction study of its crystalline benzene solvate VIII · C_6H_6 (see Fig. 1 and Table 2). The iron atom is located 1.725 Å from the Cp ring plane and has a common "piano stool" coordination. The isoxazole ring is planar, the planes of the **A** and **B** phenyl rings are inclined towards it by 53 and 46°.

In organic isoxazole derivatives the mean bond distances in the cycle are [17]: O(1)–N(2) 1.42(1), N(2)–C(3) 1.32(1), C(3)–C(4) 1.425(14), C(4)–C(5) 1.35(2), and

Table 1

IR and NMR data for VI–X

Complex	IR spectrum (cm^{-1})		^1H NMR spectrum[a], δ, ppm ($J(^1H-^1H)/J(^{31}P-^1H)$ Hz)			
	ν(C≡O)	ν(C=O)	Cp	Ph	CH_3	CH_2
VI Cp(OC)$_2$FeC=C(Ph)C(Ph)=NO	2040, 2000	–	4.04	6.90–7.92	–	–
VII Cp(OC)$_2$FeC=C(Ph)C(CO$_2$Et)=NO	2040, 1985	1730	3.88	7.08–7.34	0.84 (7.3)	3.97 (7.3)
VIII Cp(OC)(Ph$_3$P)FeC=C(Ph)C(Ph)=NO	1945	–	4.21	6.80–7.70	–	–
IX Cp(OC)(Ph$_3$P)FeC=C(Ph)C(CO$_2$Et)=NO	1940	1740	4.24 (1.3)	6.94–7.55	0.86 (6.7)	3.97 (6.7/2.0)
X Cp(OC)$_2$(Ph$_3$P)MoC=C(Ph)C(Ph)=NO	1960, 1880	–	4.78 (1.6)	6.50–7.80	–	–

[a] In C_6D_6, relative to TMS.

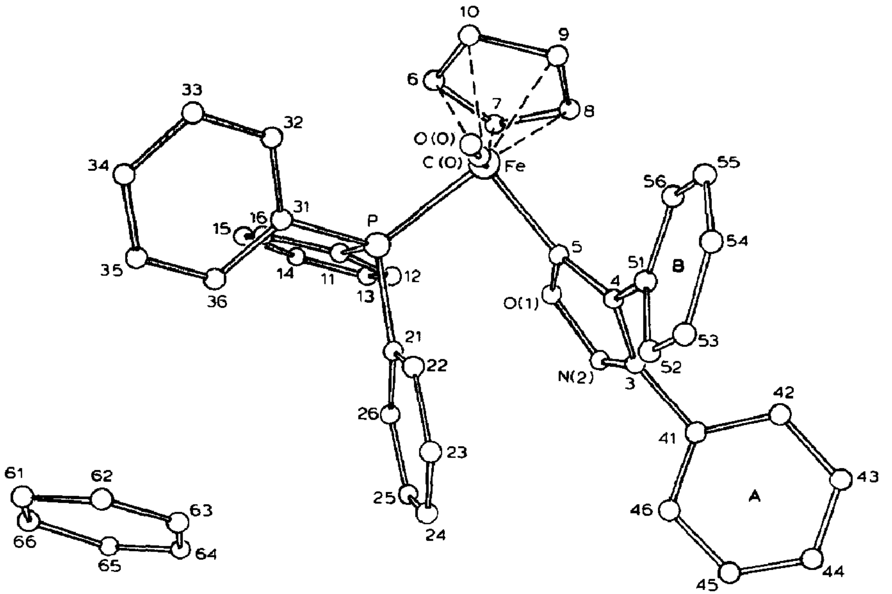


Fig. 1. Molecules of Cp(OC)(Ph$_3$P)Fe$\overline{\mathrm{C{=}C(Ph)C(Ph){=}NO}}$ (VIII) and solvating benzene in the crystal structure of VIII·C_6H_6 (H atoms are omitted).

C(5)–O(1) 1.35(1) Å. Thus the resonance form with the double N(2)=C(3) and C(4)=C(5) bonds makes the main contribution to the electronic structure of the cycle. In the isoxazole ring of VIII in the first three bonds have the same lengths as the relevant bonds quoted above, viz. 1.419(4), 1.311(4) and 1.430(5) Å, respectively, while the C(4)–C(5) and the C(5)–O(1) bonds (adjacent to the Fe–C(5) bond) are ca. 0.02 Å longer. On the other hand, though the Fe–C(5) bond distance of 1.951(3) Å lies within the common range (1.93–2.04 Å) of Fe–C(sp^2) single bonds, it is still

Table 2

Bond distances (Å) and angles (°) in VIII

Fe–P	2.212(1)	P–C(11)	1.840(3)	C(5)–O(1)	1.372(4)
Fe–C(0)	1.748(3)	P–C(21)	1.834(3)	C(3)–C(41)	1.482(5)
Fe–C(5)	1.951(3)	P–C(31)	1.837(3)	C(4)–C(51)	1.473(4)
Fe–C(6)	2.086(4)	C(0)–O(0)	1.136(4)	C(6)–C(7)	1.411(5)
Fe–C(7)	2.091(4)	O(1)–N(2)	1.419(4)	C(7)–C(8)	1.393(5)
Fe–C(8)	2.101(4)	N(2)–C(3)	1.311(4)	C(8)–C(9)	1.397(6)
Fe–C(9)	2.104(4)	C(3)–C(4)	1.430(5)	C(9)–C(10)	1.417(5)
Fe–C(10)	2.099(4)	C(4)–C(5)	1.373(4)	C(10)–C(6)	1.380(6)
PFeC(0)	92.9(1)	N(2)O(1)C(5)	110.9(2)	C(4)C(5)Fe	138.9(3)
PFeC(5)	89.3(1)	O(1)N(2)C(3)	104.0(3)	O(1)C(5)Fe	113.8(2)
C(0)FeC(5)	95.4(1)	N(2)C(3)C(4)	112.8(3)	FeC(0)O(0)	173.1(3)
FePC(11)	115.1(1)	N(2)C(3)C(41)	117.9(3)	av. CCC(Cp)	108.0(5)
FePC(21)	115.4(1)	C(4)C(3)C(41)	129.3(3)	C(12)C(11)C(16)	117.8(3)
FePC(31)	115.9(1)	C(3)C(4)C(5)	105.1(3)	C(22)C(21)C(26)	118.0(3)
C(11)PC(21)	104.9(1)	C(3)C(4)C(51)	126.2(3)	C(32)C(31)C(36)	118.6(3)
C(11)PC(31)	102.9(2)	C(5)C(4)C(51)	128.7(3)	C(42)C(41)C(46)	119.9(3)
C(21)PC(31)	100.9(1)	O(1)C(5)C(4)	107.2(3)	C(52)C(51)C(56)	118.2(3)

somewhat shorter than the mean value of 1.98 Å [18]. Thus, the observed structure of VIII exhibits a slight (within the limits of experimental error) shift towards the carbene structure with the double Fe=C(5) bond. The narrow O(1)C(5)C(4) angle of 107.2(3)° in VIII (vs. the mean value of 110(1)° in organic isoxazole derivatives) is consistent with Fe→C(5) π back-donation. In other respects the molecular geometry of VIII is unexceptional.

Isoxazoles are widely used in organic synthesis for the preparation of bifunctional organic compounds [19]. The presence of a chiral centre, such as the iron atom in the complexes VIII and IX, permits the preparation of optically active synthons.

We attempted to open the isoxazol ring in VIII and IX under the conditions commonly used for organic isoxazoles. However, VIII remains unaffected under action of butyllithium in an ethanolic solution of NaOH or $NaBH_4/NiSO_4$. Compounds VIII and IX also turned out to be inert in reactions of CO insertion into the Fe–C bond in the presence of $[Cp_2Fe]BF_4$ or $(NH_4)_2Ce(NO_3)_6$.

Experimental

Absolute solvents and L 100/400 μ silica gel were used. IR spectra were recorded with a Zeiss UR-20 spectrophotometer in KBr pellets, and ^1H NMR spectra on a Bruker WP-200-SY spectrometer operating at 200.13 MHz.

The X-ray single crystal diffraction study on VIII was carried out by use of an automated four-circle Syntex $P2_1$ diffractometer (T 20 °C, graphite-monochromated Mo-K_α radiation, $\theta/2\theta$ scan, $2\theta \leqslant 50°$, 3700 independent observed reflections with $I \geqslant 2\sigma(I)$) and calculations were performed with an Eclipse S/200 computer using INEXTL programmes [20].

Yellow crystals of $C_{39}H_{30}FeNO_2P \cdot C_6H_6$ obtained from benzene-heptane are monoclinic, space group $P2_1/n$, a 16.399(4), b 9.539(2), c 23.442(6) Å, β 98.19(2)°, V 3630 Å^3, $Z = 4$, D_c 1.30 g cm^{-3}, μ(Mo-K_α) 5.0 cm^{-1}. The structure was solved by Patterson and Fourier methods. Least squares refinement (non-hydrogen atoms anisotropic, hydrogen atoms isotropic) converged to $R = 0.041$ ($R_w = 0.038$). Weighting scheme $w = [\sigma^2(F) + 0.0001\ F_0^2]^{-1}$ was used, goodness of fit being 1.49. Atomic coordinates are listed in Table 3.

Preparation of VI. 0.28 g (1.8 mmol) of IV was added with stirring to a solution of 0.12 g (0.44 mmol) of I in benzene (40 ml), and heated to ca. 45 °C. 0.28 ml (2.0 mmol) of Et_3N was added dropwise, then heating was stopped and the mixture was stirred for 3 hours. After removal of the solvent the residue was chromatographed on silica gel. Elution with benzene gave first a mixture of I with diphenylfuroxane (DPF) as a by-product and then VI, 0.08 g (46%), isolated as yellow crystals with m.p. 119–120 °C (from petroleum ether-diethyl ether, 3 : 1). Found: C, 66.84; H, 3.80; N, 3.32; Fe, 14.17%. $C_{22}H_{15}FeNO_3$, calcd.: C, 66.52; H, 3.81; N, 3.52; Fe, 14.06%.

Preparation of VII. 0.83 g (6 mmol) of V was added with stirring to a solution of 0.33 g (1.2 mmol) of I in benzene (30 ml). The mixture was heated to ca. 45 °C, and after dropwise addition of 1.4 ml (10 mmol) of Et_3N, it worked-up as described for VI. The residue was chromatographed on silica gel, using benzene and benzene-diethyl ether (4 : 1) as eluents. At first a mixture of the initial I with DPF was eluted, and then 0.12 g (26%) of VII as an oil, whose crystallization from light petroleum

Table 3

Atomic coordinates ($\times 10^4$, for Fe and P$\times 10^5$, for H$\times 10^3$) of VIII$\cdot C_6H_6$

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Fe	15047(3)	15026(5)	38882(2)	C(56)	2323(2)	4469(4)	3039(1)
P	19949(5)	11162(9)	48033(4)	C(61)	4333(4)	1334(7)	6972(2)
O(0)	1272(2)	4449(3)	4078(1)	C(62)	3985(4)	2622(7)	6869(3)
O(1)	3050(1)	344(2)	3794(1)	C(63)	3469(3)	3141(6)	7229(3)
N(2)	3878(2)	502(3)	3693(1)	C(64)	3309(3)	2400(6)	7684(3)
C(0)	1411(2)	3305(3)	3997(1)	C(65)	3643(4)	1142(6)	7782(3)
C(3)	3929(2)	1825(3)	3551(1)	C(66)	4139(5)	583(6)	7427(3)
C(4)	3168(2)	2561(3)	3546(1)	H(6)	40(2)	−25(3)	422(1)
C(5)	2631(2)	1590(3)	3712(1)	H(7)	145(2)	−136(3)	368(1)
C(6)	536(2)	82(4)	3879(2)	H(8)	166(2)	19(4)	287(1)
C(7)	1153(2)	−504(4)	3590(2)	H(9)	58(2)	229(4)	289(2)
C(8)	1234(2)	353(4)	3120(2)	H(10)	−14(2)	189(4)	368(2)
C(9)	679(2)	1466(5)	3114(2)	H(12)	266(2)	−142(3)	443(1)
C(10)	243(2)	1279(5)	3589(2)	H(13)	268(2)	−368(3)	467(1)
C(11)	2005(2)	−734(3)	5027(1)	H(14)	193(2)	−450(3)	536(1)
C(12)	2419(2)	−1711(3)	4738(2)	H(15)	128(2)	−290(4)	588(2)
C(13)	2392(2)	−3110(4)	4867(2)	H(16)	132(2)	−55(3)	563(1)
C(14)	1958(2)	−3577(4)	5287(2)	H(22)	269(2)	377(4)	487(1)
C(15)	1548(2)	−2623(4)	5578(2)	H(23)	404(2)	469(4)	513(2)
C(16)	1575(2)	−1217(3)	5453(2)	H(24)	517(2)	321(4)	543(2)
C(21)	3049(2)	1739(3)	5034(1)	H(25)	490(2)	81(4)	551(2)
C(22)	3192(2)	3161(4)	4992(2)	H(26)	364(2)	−12(3)	528(1)
C(23)	3972(3)	3719(4)	5148(2)	H(32)	42(2)	251(3)	479(1)
C(24)	4619(2)	2848(4)	5337(2)	H(33)	−33(2)	351(4)	545(2)
C(25)	4491(2)	1460(5)	5376(2)	H(34)	27(2)	375(4)	641(1)
C(26)	3705(2)	889(4)	5231(2)	H(35)	161(2)	275(3)	667(1)
C(31)	1444(2)	1982(3)	5335(1)	H(36)	227(2)	171(4)	602(1)
C(32)	660(2)	2509(4)	5168(1)	H(42)	426(2)	316(4)	262(2)
C(33)	232(2)	3166(4)	5571(2)	H(43)	547(2)	399(4)	235(2)
C(34)	586(3)	3274(5)	128(2)	H(44)	668(2)	366(4)	300(2)
C(35)	1363(3)	2749(5)	6297(2)	H(45)	661(3)	237(4)	393(2)
C(36)	1793(2)	2121(4)	5904(2)	H(46)	540(2)	175(4)	418(1)
C(41)	4729(2)	2343(3)	3411(2)	H(52)	403(2)	483(3)	383(1)
C(42)	4771(2)	3007(4)	2893(2)	H(53)	384(2)	721(4)	366(2)
C(43)	5527(3)	3456(5)	2756(2)	H(54)	265(2)	794(4)	305(1)
C(44)	6225(3)	3216(5)	3141(3)	H(55)	171(2)	603(4)	268(1)
C(45)	6185(2)	2555(5)	3643(3)	H(56)	198(2)	373(3)	290(1)
C(46)	5437(2)	2128(5)	3793(2)	H(61)	466(4)	105(7)	664(3)
C(51)	3021(2)	4053(3)	3404(1)	H(62)	412(3)	316(6)	651(2)
C(52)	3578(2)	5077(4)	3627(2)	H(63)	322(3)	408(5)	717(2)
C(53)	3437(3)	6478(4)	3494(2)	H(64)	289(3)	307(6)	802(2)
C(54)	2733(3)	6881(4)	3145(2)	H(65)	345(4)	75(6)	810(3)
C(55)	2184(3)	5887(4)	2919(2)	H(66)	435(4)	−36(7)	746(3)

ether-diethyl ether gave pale-yellow crystals, m.p. 104–105 °C. Found: C, 58.52; H, 4.10; N, 3.46; Fe, 14.04%. $C_{19}H_{15}FeNO_5$, calcd.: C, 58.04; H, 3.85; N, 3.56; Fe, 14.20%.

Preparation of VIII. 0.91 g (5.85 mmol) of IV was added with stirring to a solution of 1.26 g (2.46 mmol) of II in 50 ml of benzene. The mixture was worked-up as described for VII, after the addition of 2.5 ml (18 mmol) of Et_3N.

After the traces of initial II had been eluted with DPF, 1.27 g (82%) of orange crystalline VIII was isolated, m.p. 190–191° C (dec.) (from benzene-diethyl ether, 1:1). Found: C, 74.15; H, 4.80; N, 2.41; Fe, 8.72%. $C_{39}H_{30}FeNO_2P$, calcd.: C, 74.18; H, 4.79; N, 2.22; Fe, 8.84%.

Preparation of IX. To a solution of 0.2 g (0.4 mmol) of II in 20 ml of benzene, was added 0.14 g (1.0 mmol) of V with stirring. The mixture was worked-up as described above, after the addition of 0.6 ml (4.3 mmol) of Et_3N. 0.23 g (94%) of orange crystalline IX was isolated, m.p. 176–176.5° (dec.) (from benzene-diethyl ether, 1:1). Found: C, 68.69; H, 4.81; N, 2.36; Fe, 9.51%. $C_{36}H_{30}FeNO_4P$, calcd.: C, 68.91; H, 4.82; N, 2.23; Fe, 8.90%.

Preparation of X. To a solution of 0.18 g (0.31 mmol) of III in 30 ml of benzene, was added 0.2 g (1.30 mmol) of IV with stirring. The mixture was worked-up as described above, after the addition of 0.2 g (1.44 mmol) of Et_3N. Elution with hexane-diethyl ether (2:1, 1:1) and benzene, 0.16 g (74%) yielded yellow crystalline X, m.p. 163–164° C (dec.) (from benzene-diethylether, 1:1). Found: C, 69.21; H, 4.24; N, 1.99%. $C_{40}H_{30}NMoO_3P$, calcd.: C, 68.67; H, 4.32; N, 2.00%.

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