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1-Allylpyrazole as a Ligand. V.[*] Preparation and Characterization of Some Iron(0) and Group VI Metal(0) Carbonyls

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The 1-allylpyrazole complexes of the general formula $Fe(CO)_3L$ (L=substituted 1-allylpyrazoles) have been prepared by the photochemical reaction of $Fe(CO)_5$ in the presence of 1-allylpyrazoles, and characterized by the IR, ^1H-, and ^{13}C-NMR spectroscopies. These complexes show a large decrease of $\nu(C=C)$ frequency and ^1H- and ^{13}C-NMR upfield shifts of the olefinic nuclei compared with free ligands. The upfield shifts of olefinic ^1H-NMR spectra are not influenced by the substituent groups on the pyrazole ring, but, so far as the terminal olefinic protons are concerned, the shifts are distinctively decreased on replacement of the allyl by the 2-methylallyl group. The upfield shifts of ^{13}C-NMR spectra substantially parallel those of ^1H-NMR spectra in these complexes. On refluxing $Fe(CO)_3L$ in a hexane solution containing PPh_3, the complex liberates 1-allylpyrazole to give *trans*-$Fe(CO)_3(PPh_3)_2$ in a small yield. Some new complexes of general formula $M(CO)_4L$ (M=Cr, Mo, or W, L=1-allylpyrazole) have also been prepared for comparison.

In order to rationalize the metal-olefin bond, Dewar, Chatt and Duncanson had postulated a model,[1] which emphasized the dual bonding nature, that is, olefin→metal σ-donation and metal→olefin π-back donation. The properties of some metal–olefin complexes have been well explicated by this model. However, many types of the olefin complexes are now accumulating, and in order to elucidate the particular bonding nature in each type of the complexes, it is important to study systematically closely related complexes.

In previous reports,[2–5] we have already prepared and characterized a large number of the 1-allylpyrazole–transition metal complexes. Thus successful preparation of these chelating-olefin complexes has so far enabled us to obtain much information concerning the particular bonding nature in each metal complex. We have now extended our study to a series of iron(0) complexes $Fe(CO)_3L$ (L=substituted 1-allylpyrazole), and spectroscopically characterized these complexes. Spectroscopic data on the isolated iron complexes are compared with those of other olefin–transition metal complexes. The effects of pyrazole substituents upon the metal–olefin and metal–carbonyl bonds are also discussed on the basis of IR and NMR data.

Experimental

All manipulations were carried out under a nitrogen atmosphere. The solvents were dried over sodium wire or lithium aluminium hydride and were distilled just before use. Metal carbonyls (Strem Chemicals or Pressure Chemicals Co.,) were used without further purification.

The IR and ^1H-NMR spectra were recorded as described previously.[5] The ^{13}C-NMR spectra were recorded on a JEOL-PET-100 Fourier Transform Spectrometer operating at 25.2 MHz with proton noise decoupling. In order to make the assignment clear, some ^{13}C-NMR spectra were obtained without decoupling. Chemical shifts were referred to the internal standard of TMS. Samples were dissolved in $CDCl_3$ as much as possible (about 20 wt%) and sealed up under an argon atmosphere.

Ligands. The ligands were synthesized from the reaction of pyrazole derivatives with allyl halide or 2-methylallyl halide. The vigorous stirring throughout the reaction generally gave a high yield of product. The boiling points and yields of ligands are summarized in Table 1.

TABLE 1. LIST OF THE 1-ALLYLPYRAZOLES

Abbreviation[a]	Bp (°C/mmHg)	Yield (%)
ap	90—100/100	66
admp	90—100/30	35
amdmp	55—62 /0.2	35
atmp	85—86 /12	48
amtmp	99—103/12—14	43
admpBr	106—107/14	57
amdmpBr	118—125/14	70
admpNO$_2$	150—151/12	63

a) ap=1-allylpyrazole, admp=1-allyl-3,5-dimethylpyrazole, amdmp=1-(2-methylallyl)-3,5-dimethylpyrazole, atmp=1-allyl-3,4,5-trimethylpyrazole, amtmp=1-(2-methylallyl)-3,4,5-trimethylpyrazole, admpBr=1-allyl-4-bromo-3,5-dimethylpyrazole, amdmBr=1-(2-methylallyl)-4-bromo-3,5-dimethylpyrazole, amdmpNO$_2$=1-allyl-3,5-dimethyl-4-nitropyrazole.

Group VI Metal Complexes, $M(CO)_4(ap)$ (M=Cr, Mo, or W, ap=1-allylpyrazole). The group VI metal complexes $M(CO)_4(ap)$ were prepared as described already.[5] They were sparingly soluble in hexane and were recrystallized from diethyl ether–hexane.

Tricarbonyl-1-allypyrazoleiron(0), $Fe(CO)_3(C_6H_8N_2)$. The iron complexes were obtained in a similar manner to the group VI metal complexes. A tetrahydrofuran solution (300 ml) containing both pentacarbonyliron(0) (2.0 g, 0.01 mol) and allylpyrazole (1.1 g. 0.01 mol) was irradiated with a mercury lamp (400 W). The flask(Riko, UVL-400 HA) was equipped with a gas buret to follow the course of the reaction. In 3—4 h, the reaction was completed showing the stoichiometric evolution of CO. The amber-colored solution was evacuated to dryness and the resulting residue was completely extracted with hexane(100 ml) at room temperature. The hexane solution was filtered and condensed to half a volume *in vacuo*. On cooling the solution at −78 °C, yellow fine crystals were deposited in a yield of 80% (2.0 g). The product was purified by the repeated recrystallization from hexane.

Similarly the iron(0) complexes containing substituted 1-allylpyrazole were prepared as listed in Table 2. The complexes are soluble in most organic solvents usually used. In

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[*] Part IV, see Ref. 5.

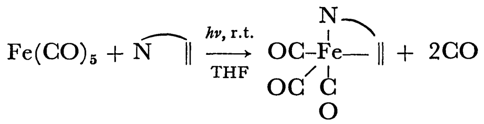
a crystalline form, they are fairly air-stable, but in a solution they are rapidly decomposed by contact with air.

No solid product was obtained in the reaction of $Fe(CO)_5$ with 1-allyl-3,5-dimethyl-4-nitropyrazole, in spite of the excessive generation of CO gas.

Reaction of $Fe(CO)_3(ap)$ with PPh_3. A hexane solution containing $Fe(CO)_3(ap)$(0.3 g, 1.2 mmol) and triphenylphosphine (1.2 g, 4.6 mmol) was refluxed for 5 h. On standing, yellow crystals are formed to give a yield of 0.3 g. The product was identified to be *trans*-$Fe(CO)_3(PPh_3)_2$ by IR and elemental analysis. IR data in $CHCl_3$: 1886(s) [lit,[6] 1887 (s)] cm^{-1}.

Results and Discussion

King and coworkers[7] isolated the complexes $Fe(CO)_3(ap)$ and $Fe(CO)_3(admp)$ (ap=1-allylpyrazole, admp=1-allyl-3,5-dimethylpyrazole), firstly as by-product of the reaction of (π-allyl)$Fe(CO)_3I$ with potassium monohydridotris(1-pyrazolyl)borate or potassium monohydridotris(3,5-dimethylpyrazolyl)borate, and subsequently as main products of the thermal reaction of $Fe_2(CO)_9$ with the ligands (ap or admp). However, those iron complexes were not fully characterized. In our experiment, the iron complexes have been synthesized quite smoothly by the photochemical reactions of $Fe(CO)_5$ with the 1-allylpyrazole ligands, in the same way as the group VI metal carbonyl complexes.[5]



^{1}H-NMR and IR Spectra. Although a great number of iron-olefin complexes have so far been prepared,[8] the infrared spectrum, which is one of the most important criteria of the metal–olefin bond, have been curiously ignored in literatures. The IR band ν(C=C) for the iron complexes $Fe(CO)_3L$ (L=1-allylpyrazole) was tentatively assignable in comparison with the spectra of the chromium(0) analogues $Cr(CO)_4L$ in the region of 1400—1600 cm^{-1}. The lowered shifts $\Delta\nu$(C=C) for the iron complexes were determined to be *ca.* 180 cm^{-1}. This abnormally large shift of ν(C=C) well agreed with the large NMR upfield shifts of the olefinic

TABLE 2. ELEMENTAL ANALYSES AND (CO) FREQUENCIES

	C	H	N	Mp (°C)	(CO) (cm^{-1})[a]
$Cr(CO)_4(ap)$[b]	44.14(44.13)	3.12(2.96)	10.21(10.29)	97—99	2029, 1950, 1931, 1895
$Mo(CO)_4(ap)$	38.03(37.99)	2.76(2.55)	9.16(8.86)	95—98	2039, 1952, 1939, 1896
$W(CO)_4(ap)$	29.99(29.73)	2.22(2.00)	7.21(6.93)	116—119	2038, 1948, 1935, 1894
$Fe(CO)_3(ap)$	43.84(43.58)	3.38(3.25)	11.65(11.30)	65—66	2039, 1964, 1956
$Fe(CO)_3(admp)$	47.96(47.86)	4.50(4.38)	10.26(10.15)	60—61	2035, 1961, 1950
$Fe(CO)_3(amdmp)$	49.88(49.68)	4.89(4.86)	9.33(9.66)	53—54	2031, 1957, 1948
$Fe(CO)_3(atmp)$	49.93(49.68)	4.54(4.86)	9.78(9.66)	105—106	2032, 1960, 1949
$Fe(CO)_3(amtmp)$	51.67(51.34)	5.49(5.30)	9.12(9.21)	35	2030, 1956, 1947
$Fe(CO)_3(admpBr)$	37.03(37.22)	2.83(3.12)	7.64(7.89)	115—118	2036, 1963, 1954
$Fe(CO)_3(amdmpBr)$	38.88(39.06)	3.70(3.55)	7.30(7.59)	83—85	2033, 1960, 1951

a) Hexane solution. b) Abbreviations are shown in Table 1.

TABLE 3. ^{1}H-NMR CHEMICAL SHIFTS OF THE OLEFINIC PROTONS (in ppm)

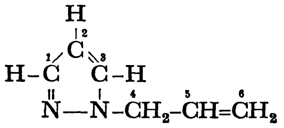
	$H_f(\Delta H_f)$[a]	$H_g(\Delta H_g)$	$H_h(\Delta H_h)$	$\lvert J_{fg}\rvert$	$\lvert J_{fh}\rvert$	Solv.
ap	5.97	5.18	5.11	10	17	$CDCl_3$
$Cr(CO)_4(ap)$	4.71(−1.26)	3.25(−1.93)	2.74(−2.37)	9	12	CS_2
$Mo(CO)_4(ap)$	4.96(−1.01)	3.51(−1.67)	3.29(−1.82)	9	13	CS_2
$W(CO)_4(ap)$	b)	3.27(−1.91)	2.74(−2.37)	9	12	CS_2
$Fe(CO)_3(ap)$	3.69(−2.28)	2.17(−3.01)	1.27(−3.84)	8	10	CS_2
admpBr	5.96	5.27	5.08	10	18	$CDCl_3$
$Fe(CO)_3(admpBr)$	3.72(−2.24)	2.11(−3.16)	1.28(−3.80)	b)	11	CS_2
admp	5.80	5.01	4.82	10	17	$CDCl_3$
$Fe(CO)_3(admp)$	3.76(−2.04)	2.15(−2.86)	1.31(−3.51)	b)	10.5	CS_2
atmp	5.81	5.03	4.85	10	17	$CDCl_3$
$Fe(CO)_3(atmp)$	3.70(−2.11)	2.07(−2.96)	1.27(−3.58)	7	10	CS_2
amdmpBr	—	4.82	4.49	—	—	$CDCl_3$
$Fe(CO)_3(amdmpBr)$	—	2.18(−2.64)	1.42(−3.07)	—	—	CS_2
amdmp	—	4.80	4.48	—	—	$CDCl_3$
$Fe(CO)_3(amdmp)$	—	2.18(−2.62)	1.44(−3.04)	—	—	CS_2
amtmp	—	4.73	4.49	—	—	$CDCl_3$
$Fe(CO)_3(amtm)$	—	2.14(−2.59)	1.41(−3.08)	—	—	CS_2

a) The symbol ΔH represents the difference in chemical shifts between a proton in an iron complex and one in a free ligand. b) Not measurable by overlapping.

Table 4. ^{13}C-NMR data of some 1-allylpyrazole (ap) complexes
(Solvent; CDCl$_3$, in δ_{ppm} from TMS)

Compound	Ring$^{a)}$			Allyl$^{a)}$			Carbonyl	$\Delta\nu$(C=C)$^{b)}$ (cm^{-1})
	C^1	C^2	C^3	C^4	C^5	C^6		
Free ligand	138.7	105.2	128.5	54.1	132.7	117.7		—
	(184.3)	(175.8)	(185.6)	(138.4)	(162.3)	(153.4)		
Cr(CO)$_4$(ap)	142.6	107.7	130.8	52.0	77.4	64.2	230.7, 224.3, 223.6, 223.5	131
	(185.5)	(179.9)	(186.8)	(142.9)	(168.5)	(167.4)		
Mo(CO)$_4$(ap)	143.3	107.4	131.0	53.0	81.2	67.2	218.6, 217.9, 210.3, 209.6	119
W(CO)$_4$(ap)	143.3	107.8	130.9	52.3	69.7	56.1	212.8, 208.6, 204.0, 203.0	138
Fe(CO)(ap)	142.0	108.2	130.3	55.0	48.3	36.0	213.1	189
	(189.7)	(180.5)	(189.5)	(137.7)	(160.6)	(158.1)		

a) $|J_{C-H}|$ in parentheses.
b) Lowered shifts of ν(C=C) measured in KBr disks.



protons. The observed value $\Delta\nu$(C=C) of about 180 cm^{-1}, as well as the value of the upfield shifts $\Delta\delta$H of 2.2—3.8 ppm were much larger than those of the chromium(0) complexes ($\Delta\nu$(C=C): 120 cm^{-1}, $\Delta\delta$H: 1.0—2.4 ppm). Tolman and coworkers[9] tabulated the spectroscopic data on the many ethylene–transition metal complexes. According to the table, it can be clearly shown that the iron(0)-olefin interaction is classified as the largest, and the chromium(0)-olefin one as the medium.

Through a series of the iron complexes, Fe(CO)$_3$L, the increase of the methyl sibstituents on the pyrazole ring caused a substantial decrease of the ν(C≡O) frequencies as shown in Table 2, but did not give significant changes in the final chemical shifts for the olefinic protons (Table 3), regardless of the fairly different chemical shifts of the free ligands. These results indicate that the metal-olefin bond in these iron complexes has a lower sensitivity towards the methyl substitution on the pyrazole ring, compared with the metal-carbonyl bond. The increase in the σ-donor ability of the *N*-coordinating site owing to the methyl substituents seems to promote the π-delocalization to the carbonyl moiety, but not to the olefinic group.

^{13}C-NMR Spectra. The ^{13}C-NMR spectral data for the four 1-allylpyrazole (ap) complexes are listed in Table 4 together with the shift data of the stretching frequencies of ν(C=C). The shift difference between the two olefinic carbons decreased as a result of coordination of the olefinic part in ap, compared with free ap; such a case had already been reported by Brown.[10] The ^{13}C-NMR spectra due to the olefinic carbons as a whole shifted towards a higher magnetic field from the position of the free ligands as described in the case of ^{1}H-NMR spectra. Though ^{13}C-NMR spectral data of other group VI metal–olefin complexes are not available, the observation that the ^{13}C-NMR chemical shift of the M(CO)$_4$L, where M=Cr, W, and L=ap move upfield when chromium is replaced by tungsten may be consistent with the stronger olefin–metal bond present in the tungsten complex.

While each group VI metal carbonyl complexes showed the four carbonyl carbon resonances, only one signal was found for three unequivalent carbonyls of the iron complex. As has been reported in detail by several workers,[11] it indicates the high fluctionality of the iron carbonyl complexes. The carbonyl carbon resonance for the group VI metal complexes have the following order of deshielding as: Cr>Mo>W. This is the same order as that observed in the parent hexacarbonyls M(CO)$_6$ and a series of pentacarbonyl complexes, M(CO)$_5$L (M=Cr, Mo, or W, L=a unidentate ligand).[12]

Displacement Reaction of the Coordinated Ligand. The great tendency to the displacement of the coordinated *N*-allylpyrazole by the strong donor ligands has been the most remarkable feature for the Pt(II), Cr(0), and Mo(0) complexes.[3,5] The iron(0) complex Fe(CO)$_3$L, however, did not react with PPh$_3$ under mild conditions. Only after refluxing both reagents in a hexane solution for several hours, the complex, *trans*-Fe(CO)$_3$(PPh$_3$)$_2$ was obtained in a low yield. The lability of the coordinated ap ligand in the iron complex is obviously lower than that in the chromium complex Cr(CO)$_4$(ap).

Metal–Olefin Bond Strength. The correlation between the NMR upfield shifts and the metal-olefin bond nature has not been confirmed yet.[13] One research group attributed it to the paramagnetic shielding effect induced by the non-bonding partially filled d-orbitals,[14] while the other group to the magnitude of the π-bond order due to the π-back donation.[15] Our results support the latter one, since so far as iron(0) and the group VI metals(0) concerned, the large NMR upfield shifts were always accompanied by the larger decrease in the ν(C=C) frequencies and the lower activity of the displacement of the coordinated olefinic ligand, *i.e.*, in the order of Fe>W>Cr>Mo. This result that iron(0) is more strongly bonded to the olefin than chromium(0) by the larger π-back bonding will support Hoffmann's MO calculations of the metal carbonyl fragments.[16]

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