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N-ALLYLPYRAZOLE AS A LIGAND

IV *. PREPARATION AND CHARACTERIZATION OF THE *N*-OLEFIN CHELATE COMPLEXES WITH GROUP VI METAL(0) CARBONYLS

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Summary

Reaction of 1-allyl-3,5-dimethylpyrazole (ADMP) with Group VI metal hexacarbonyls, $M(CO)_6$ (M = Cr, Mo, W), under photoirradiation yielded novel mono-olefin complexes of the general formula $M(CO)_4(ADMP)$, in which both pyrazolyl-*N* and the olefinic part of the allyl group are coordinated to the metal in a *cis*-configuration. The coordinated olefinic group showed ^1H NMR upfield shifts, a decrease of the C=C vibration frequencies from those of the free ligand. The ligand *N*-allylpyrazole coordinated to Cr and Mo was found to be easily displaced by other donor ligands such as tertiary phosphines. The displacement reactions provided a convenient route for the preparation of the *cis*- or *trans*-disubstituted tetracarbonyl complexes of these metals.

Introduction

Metal carbonyls are known to catalyze the isomerization of olefins, especially under photo-irradiation [2]. The catalytic reactions are considered to proceed via complexes of the olefins with these metals. But the intermediates, simple mixed mono-olefin—carbonyl complexes, are in general unstable and it requires the additional coordination of another ligand such as a tertiary phosphine or arsine to give a stable complex [3]. Bennett and co-workers have succeeded in preparing stable mono-olefin complexes with many transition metal carbonyls, using phosphine-olefin and arsine-olefin types of bidentate ligands [4-10]. Since phosphines and arsines are able to utilize empty *d*-orbitals which can accept the π-back-donation from the metal to lower the overall energy [11], the stabilizing effect of above phosphine-olefin and arsine-olefin ligand complexes appears to be due to the π-acceptor properties of the donor atoms themselves,

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* Part III: ref. 1.

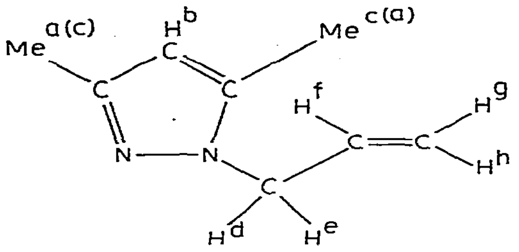

Fig. 1. 1-Allyl-3,5-dimethylpyrazole.

as well as to the chelate effect. On the other hand, when the donor is a nitrogen atom, which cannot use vacant *d*-orbitals, only heterocyclic aromatics and imino groups, etc., show a weak π-acceptor ability. In fact, only restricted kinds of olefin—carbonyl complexes stabilized by an *N*-ligand are known, e.g., $[Fe(CO)_3(acrylonitrile)]_2$ [12].

From this point of view, it was of interest to investigate the complexing ability of *N*-allylpyrazole with metal carbonyls. King and co-workers have isolated $Fe(CO)_3$(1-allylpyrazole) as a by-product of the reaction of tris(pyrazolyl)borate anion with (π-allyl)$Fe(CO)_3I$ and confirmed it with the reaction of 1-allylpyrazole and $Fe_2(CO)_9$ [13]. Previously, we prepared several *N*-allylpyrazole (Fig. 1) complexes with some transition metals in normal oxidation states, whereby stable olefin complexes with copper(I), silver(I) [14], palladium(II) and platinum(II) [15] were obtained. The crystal structure of the copper(I) complex showed that the ligand coordinates to the metal as a nitrogen-olefin chelate [1].

In this report, the preparation and the characterization as well as the displacement reactions of the first nitrogen-olefin chelate type complexes of Group VI metal carbonyls, $M(CO)_4$(ADMP) (M = Cr, Mo, W; ADMP = 1-allyl-3,5-dimethylpyrazole) are described.

Experimental

Infrared spectra were recorded on a Hitachi EPI—G2 spectrophotometer in n-hexane or chloroform solution and in KBr disks. ^1H NMR spectra were recorded on a JEOL PS—100 instrument (100 MHz) in carbon disulfide solution, using TMS as an internal standard.

Starting materials

The ligand 1-allyl-3,5-dimethylpyrazole (ADMP) was prepared as previously described [14]. Metal hexacarbonyls were commercially available and used without further purification. The solvents tetrahydrofuran and n-hexane were distilled over sodium wire and deaerated before use. All the procedures for the isolation of the complexes were undertaken under a nitrogen atmosphere.

Preparation of complexes

1. Photo-irradiation method. A solution of 0.01 mol of a metal hexacarbonyl and 0.01 mol of ADMP in 400 ml of THF was stirred for 5 min in a flask and

TABLE 1

ELEMENTAL ANALYSES AND IR DATA OF THE COMPLEXES

Complex	Color	M.p. (°C)	Yield (%)	C [a]	H	N	ν(C≡O) [b] (cm^{-1})	ν(C=C) [c] (cm^{-1})
$Cr(CO)_4$(ADMP)	yellow	108—110	57	48.45 (48.01)	4.19 (4.03)	9.50 (9.34)	2027m 1941vs 1924vs 1891vs	1522
$Mo(CO)_4$(ADMP)	dark-yellow	103—105	44	41.99 (41.87)	3.49 (3.51)	7.93 (8.14)	2040 1943 1925 1893	1520
$W(CO)_4$(ADMP)	yellow	116—118	50	33.21 (33.36)	2.52 (2.80)	6.53 (6.48)	2030 1935 1925 1886	1512

[a] Calculated value in parentheses. [b] n-Hexane solution. [c] KBr disk.

was then transferred to a photo-irradiation apparatus (Riko UVL—400HA, 400 W, made of pyrex glass). The reaction vessel was equipped with a nitrogen inlet and connected to a gas-buret. In 2 h of irradiation, evolution of CO gas almost ceased after about 0 015 mol had been evolved. Further irradiation for 2 h showed only a negligible increase of evolved gas. The solvent was removed from the yellow solution by evaporation in vacuo at room temperature, and the yellow crystalline residue was extracted with 200 ml of hexane. The hexane solution was concentrated to about 70 ml by evaporation in vacuo and cooled gradually in an ice-bath for crystallization. The yellow crystals were purified by several repetitions of this procedure. The final crystals were dried thoroughly in vacuo to sublime away the unreacted hexacarbonyl. The yields after two recrystallizations are shown in Table 1.

2. *Thermal method.* The Mo complex was also obtained by the thermal reaction of $Mo(CO)_6$ and ADMP in hexane solution. A mixture of $Mo(CO)_6$ (5 mmol) and an equimolar amount of ADMP in 300 ml of hexane was refluxed with stirring. The course of the reaction was monitored with a gas-buret. In about 4 h, gas-evolution corresponding to 6 mmol was noted. The solution became yellow and dark brown, oily precipitates appeared on the wall. The solution was filtered and cooled in an ice-bath. The product was purified as described above. Yield: 12%.

The complexes are all air-stable and dissolve in most organic solvents but not in water. The complexes in solution gradually decompose when in contact with air. Elemental analyses and some properties are summarized in Table 1.

Displacement reactions

Case 1. (M = Cr, Mo; L = PPh_3, pyridine). The complex $M(CO)_4$(ADMP) (1 mmol) was dissolved in 100 ml of hexane and an excess of L (> 2 mmol) was added with stirring. Immediately, pale-yellow or orange crystals were formed in almost quantitative yield. These reactions could be carried out in air. Physical properties examined to identify the products are summarized here, since these data are scattered in several reports and are not always in agreement with each other; *trans*-$Cr(CO)_4(PPh_3)_2$; Anal. Found: C, 69.70; H, 4.85. $C_{40}H_{36}CrO_4P_2$ calcd.: C, 69.77; H, 4.39%; m.p. 158—160°C; ν(CO)($CHCl_3$) 1946 cm^{-1} w, 1885vs. *cis*-$Mo(CO)_4(PPh_3)_2$; Anal. Found: C, 65.61; H, 4.04. $C_{40}H_{30}MoO_4P_2$ calcd.: C, 65.52; H, 4.10%; m.p. 165—168°C; ν(CO)($CHCl_3$) 2024 cm^{-1} m, 1926vs, 1910vs, 1890vs. *cis*-$Cr(CO)_4Py_2$; Anal. Found: C, 52.05; H, 2.84; N, 8.99.

$C_{14}H_8CrN_2O_4$ calcd.: C, 52.18; H, 2.13; N, 8.69%; m.p. >75°C dec. without melting; ν(CO)(KBr) 2000m, 1906vs, 1865vs, 1820vs. *cis*-Mo(CO)$_4$Py$_2$; Anal. Found: C, 45.82; H, 2.54; N, 7.84. $C_{14}H_8MoN_2O_4$ calcd.: C, 45.50; H, 2.73; N, 7.65%; m.p. >75°C dec. without melting; ν(CO)(KBr) 2003m, 1920vs, 1877vs, 1827vs.

Case 2. (M = Cr, Mo; L = P(OPh)$_3$). In this case, the reaction was carried out in ethanol solution. In a few hours, faintly colored crystals were obtained after adding an adequate amount of n-hexane to the almost colorless solution. Identification of products; *trans*-Cr(CO)$_4$[P(OPh)$_3$]$_2$; Anal. Found: C, 61.00; H, 4.01. $C_{40}H_{30}CrO_{10}P_2$ calcd.: C, 61.22; H, 3.83%; m.p. 150—151°C; ν(CO)(CHCl$_3$) 1935vs. *cis*-Mo(CO)$_4$[P(OPh)$_3$]$_2$; Anal. Found: 58.11; H, 3.81. $C_{40}H_{30}MoO_{10}Pz$ calcd.: 57.99; H, 3.65%; m.p. 106—108°C; ν(CO)(CHCl$_3$) 2045m, 1957vs, 1936vs(br).

Case 3. (M = Cr, L = PCy$_3$, AsPh$_3$; M = Mo, L = AsPh$_3$).* The photo-irradiation was quite effective and with 30 min of irradiation, the yields rose to 70—90% from 5—25% with the reaction set as in Case 1, for a few days. Identification of products; *trans*-Cr(CO)$_4$(PCy$_3$)$_2$; Anal. Found: C, 66.19; H, 9.34. $C_{40}H_{66}CrO_4P_2$ calcd.: C, 66.30; H, 9.12%; m.p. 164—168°C; ν(CO)(CHCl$_3$) 1915w, 1854vs. *cis*-Cr(CO)$_4$(AsPh$_3$)$_2$; Anal. Found: C, 62.17; H, 3.67. $C_{40}H_{30}As_2CrO_4$ calcd.: C, 61.87; H, 3.89%; m.p. 138—141°C; ν(CO)(CHCl$_3$) 2010m, 1918s(sh), 1892vs(br). *cis*-Mo(CO)$_4$(AsPh$_3$)$_2$; Anal. Found: C, 58.83; H, 3.79. $C_{40}H_{30}As_2MoO_4$ calcd.: C, 58.56; H, 3.69%; m.p. 157—160°C; ν(CO)(CHCl$_3$) 2026m, 1928vs, 1913vs, 1888vs.

Case 4. (M = Mo, L = PCy$_3$). With these reactants, no products were obtained following the method described in Case 3. Photo-irradiation was not effective and the reaction occurred only on heating. A hexane solution of Mo(CO)$_4$(ADMP) and PCy$_3$ was refluxed for 3 h and set aside at room temperature. Pale-yellow crystals were obtained in a 45% yield. Identification of product; *trans*-Mo(CO)$_4$(PCy$_3$)$_2$; Anal. Found: C, 62.07; H, 9.11. $C_{40}H_{66}MoO_4P_2$ calcd.: C, 62.49; H, 8.65%; m.p. 213—215°C; ν(CO)(CHCl$_3$) 2000vw, 1925w, 1865vs.

Results and discussion

The nitrogen-olefin chelate, 1-allyl-3,5-dimethylpyrazole (ADMP), reacted with M(CO)$_6$ (M = Cr, Mo, W) under photoirradiation to yield stable complexes of the formula M(CO)$_4$(ADMP) selectively:

$$\mathrm{M(CO)_6 + ADMP \xrightarrow[THF]{h\nu} M(CO)_4(ADMP) + 2CO}$$

It was established from the IR and the ^{1}H NMR spectra that the ADMP complexes are coordinated through both the pyrazole nitrogen and the olefinic part of the allyl group in *cis*-configuration. The ν(C=C) band, found at 1646 cm^{-1} in the free ligand, disappeared in the complex and instead a new band appeared in the vicinity of 1510—1520 cm^{-1} which can be assigned tentatively to the shifted ν(C=C). The ^{1}H NMR signals of the olefinic protons were shifted to higher field by 1—2 ppm. As observed in the diphenyl(prop-2-enyloxo)phosphinerhodium(I)

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* Cy = cyclohexyl.

complex [16], the terminal methylene proton H(h) shows the largest shift (1.6—2.2 ppm) and the methyne proton H(f) shows the smallest (0.8—1.3 ppm). The spin—spin coupling constants among the olefinic protons, $|J_{fg}|$ and $|J_{fh}|$, show distinct decreases upon coordination. In addition, the coordination is accompanied by a splitting of the methylene protons H(d) and H(e), which are coincident in the free ligand. The geminal coupling constant $|J_{de}|$ is about 14 Hz. The splitting is supported by the structural analysis of $[CuCl(ADMP)]_2$, which indicates different environments of the two hydrogens upon coordination [1]. A similar splitting has been found in the above cited rhodium(I) complex [16].

$\nu(C{\equiv}O)$ are listed in Table 1. The four strong bands expected for a *cis*-disubstituted tetracarbonyl are found. Although Bennett and co-workers [10] have suggested two rotational isomers by observing the complicated $\nu(C{\equiv}O)$ in molybdenum and tungsten phosphine-olefin and arsine-olefin complexes, no such complexity was found in ADMP complexes, not only for Cr but also for Mo and W compounds. This is probably because of thermal motion or the existence of only one conformation. These data agree with the predicted structure resembling that of $Mo(CO)_4$[(*o*-propenylphenyl)diphenylphosphine] [17], but leaving the rotational direction of the coordinated C=C moiety unknown (Fig. 2).

Despite the fact that the pyrazole ring is isoelectronic with the pyridine ring and hence may well have some π-acceptor ability, the ^{1}H NMR signals of the H and the methyl group on the ring are scarcely shifted upon coordination. This indicates that the coordination of the pyrazole nitrogen is almost entirely attributable to the σ-donation of the *N*-donor. It is interesting that the ADMP complex has a comparable thermal stability to the corresponding P—olefin and the As—olefin complexes, in spite of the significantly different character of the donor atoms.

Some differences are also found. The first difference is in the synthesis of the chelate-olefin complexes. An attempt to prepare the P—olefin complex photochemically failed and resulted in the formation of the simple tertiary phosphine complexes, $Mo(CO)_5L$ and $Mo(CO)_4L_2$ [18]. Conversely, the thermal excitation which was successfully employed for the preparation of the P—olefin complexes [6], was proved to be ineffective for the preparation of the ADMP complexes except for that of Mo, where $Mo(CO)_4(ADMP)$ was obtained in low yield. The second difference is in the properties of the ligand as reflected in the C≡O stretching vibration frequencies, $\nu(C{\equiv}O)$. These are as a whole lower than those

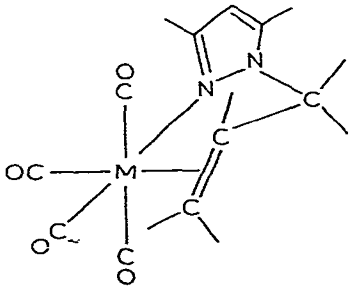


Fig. 2. Schematic molecular structure of $M(CO)_4(ADMP)$.

TABLE 2

^{1}H NMR SPECTRAL DATA (δ (ppm), Hz)

Complex	H(a) [a]	H(b)	H(c)	H(d)	H(e)	H(f)	H(g)	H(h)	$\lvert J_{de}\rvert$	$\lvert J_{df}\rvert$	$\lvert J_{fg}\rvert$	$\lvert J_{fh}\rvert$
$Cr(CO)_4(ADMP)$	2.11s	5.63	2.15	4.33d.d	4.57d	4.7m	3.22d	2.67d	13.5	4	9	13
$Mo(CO)_4(ADMP)$	2.14	5.74	2.22	4.30	4.60	4.97	3.43	3.15	13	4	8	14
$W(CO)_4(ADMP)$	2.16	5.73	2.24	4.29	4.81	4.5	3.14	2.58	14	4	8	12
Free ADMP	2.06s	5.65s	2.09s	4.46d		5.80m	5.01d	4.82d		6	10	17

[a] Notations are following Fig. 1.

in the P—olefin and As—olefin chelate complexes [10] and higher than those in the *N—P* type mixed bidentate *o-N,N*-dimethylaminophenyldiethylphosphine complexes [19] for any of these three metals. This may reflect a π-acceptor ability of ADMP lower than that of the P—olefin or the As—olefin and higher than that of the N—P ligand. The third difference is the high lability of the ADMP complex.

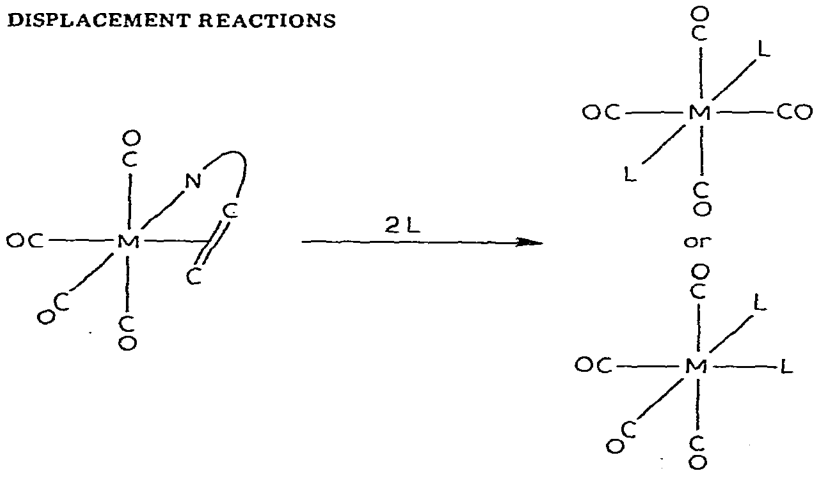
With these several donor-olefin ligands, a comparison of the bond strength of the metal-olefin among the Cr, Mo and W complexes might be possible. As shown in Tables 1 and 2, $\Delta\nu(C{=}C)$ are in the order W > Mo > Cr and the ^{1}H NMR spectra show the order of the upfield shifts of the olefinic protons to be W > Cr > Mo and that of the splitting of H(d) and H(e) to be W > Mo > Cr. In both the P—olefin and the As—olefin complexes, ^{1}H NMR upfield shifts have been found to be in the order Cr > W > Mo [10]. The meaning of the discrepancy in the orderings is ambiguous. However, it is very likely that in ADMP complexes, the metal—ligand interaction is strongest in the W complex, as observed in the catalytic isomerization of olefins [20] and this results in the distinct inertness of the W complex to displacement of the coordinated ADMP.

Displacement reactions of ADMP by N-, P- and As-donor ligands

The ligand ADMP coordinated to Cr and Mo was found to be easily displaced by some donor ligands at room temperature (Scheme 1). This provides a new

SCHEME 1

DISPLACEMENT REACTIONS



and convenient route for the preparation of certain di-substituted tetracarbonyl derivatives of these metals. The chromium complex, $Cr(CO)_4(ADMP)$, on treatment with L = $P(OPh)_3$, PPh_3 and PCy_3 gave *trans*-$Cr(CO)_4L_2$, while with L = $AsPh_3$ and pyridine gave *cis*-$Cr(CO)_4L_2$. The molybdenum complex, $Mo(CO)_4$-(ADMP), reacted with L = $P(OPh)_3$, PPh_3, $AsPh_3$ and pyridine to give *cis*-Mo-$(CO)_4L_2$, and in the case of L = PCy_3, which was the only case where heating was required, *trans*-$Mo(CO)_4(PCy_3)_2$ was obtained. The tungsten complex, $W(CO)_4(ADMP)$, however, was very inactive to the displacement. The very small amount of products of the reactions with PPh_3 and pyridine, which have not been absolutely identified, were presumed to be $W(CO)_3(ADMP)(PPh_3)$ ($\nu(C{\equiv}O)$ 1957, 1880, 1816 cm^{-1} ($CHCl_3$)) and *cis*-$W(CO)_4(Py)_2$ ($\nu(C{\equiv}O)$ 2001, 1908, 1866, 1818 cm^{-1} (KBr)).

There have been many studies of the preparation of Group VI metal carbonyl derivatives using thermal and photoexcitation [21]. To obtain di-substituted derivatives selectively, indirect displacement reactions are favored and labile diolefin, e.g., 2,5-norbornadiene, complexes have been used as the starting compound [22,23]. Our ADMP complexes are very suitable for this purpose. The ligand ADMP is easily synthesized and the complexes are obtained in high yields. They are air-stable in crystalline form and can often even be handled in air in non-polar organic solvents. When hexane was used as a solvent, the displaced product was obtained at room temperature as crystals, which were easily separated from the starting complex and L′ both of which remained in solution. More noticeable is the high lability of ADMP. It is known that similar 2,2′-bipyridine and *o*-phenanthroline complexes on treatment with PPh_3 undergo displacement of CO groups rather than of the bidentate ligand [24]. Even in the norbornadiene complex, $Cr(CO)_4(NBD)$, which undergoes thermal displacement of the diene by PPh_3, the replacement of CO was found under photo-irradiation to give $Cr(CO)_3(NBD)(PPh_3)$ [25]. In ADMP complexes, so far as the Cr and Mo complexes are concerned, neither heating nor photo-irradiation caused the elimination of CO. In addition, in palladium(II) and platinum(II) complexes, a 1-methallyl-3,4,5-trimethylpyrazole (AmTMP) ligand is known to be displaced stepwise and some mixed complexes of type $MCl_2(AmTMP)L$ have been obtained, in which AmTMP is coordinated through the pyrazolyl-*N* leaving the olefinic C=C bond free [15]. However, the equimolar reaction of $Cr(CO)_4(ADMP)$ and PPh_3 in benzene yielded only *trans*-$Cr(CO)_4(PPh_3)_2$. A mixed complex, such as $Cr(CO)_4(ADMP)(PPh_3)$, was not detected and ADMP was completely displaced. All these observations indicate that ADMP is more readily displaced than are the other bidentate ligands cited above.

The *cis*-configuration of the metal carbonyl moiety was not neccessarily obtained directly in the displacement reaction. This is considered to be due to the relative stabilities of the two configurations which are governed mainly by the steric effects, i.e., the size of the metal atom and the entering ligand [26]. When a bulky PCy_3 was reacted with $Mo(CO)_4(ADMP)$, *cis*-$Mo(CO)_4(PCy_3)_2$ could not be obtained and only with the application of heat was *trans*-$Mo(CO)_4(PCy_3)_2$ obtained. The greater stability of the *trans*-configuration has been suggested by the direct preparation of *trans*-$M(CO)_4(PCy_3)_2$ for Cr, Mo and W [27]. Hence the heating required for the preparation of $Mo(CO)_4(PCy_3)_2$ in our case may provide the activation energy for the transformation of the configuration. For

Cr, not only PCy_3 but also $P(OPh)_3$ and PPh_3 showed the *trans*-orientation, probably because of its smaller metal size and a lower energy barrier to the transformation of the configuration.

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