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THE ^{19}F NMR STUDY OF ELECTRONIC EFFECTS IN σ-PHENYL DERIVATIVES OF π-CYCLOPENTADIENYL CARBONYLS OF MOLYBDENUM AND TUNGSTEN

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SUMMARY

Six novel *p*- and *m*-fluorophenyl derivatives of cyclopentadienyl carbonyls of molybdenum and tungsten have been synthesized and their ^{1}H and ^{19}F NMR spectra investigated. The σ_R^0 and σ_I constants for these compounds as estimated from the Taft equation had negative values, indicating that metal carbonyl substituents display donor inductive and resonance effects with respect to the phenyl ring, the resonance component being rather small in the ground state.

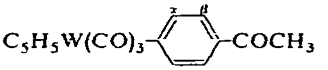
The electronic effects of organometallic substituents have recently been the subject of many studies, and in view of these studies the need to determine the ability of the metal to participate in π-bonding with aromatic ring systems has become most significant.

In such interactions the metal may be an electron acceptor (when some of its vacant orbitals (d_π for example) and the π-orbitals of the occupied benzene ring interact), or it may behave as a donor (when the occupied metal orbitals interact with vacant antibonding π^*-ring orbitals). In determining the nature of such interaction, the use of the Taft approach which allows the over-all substituent effect to be resolved into its inductive and resonance components has been found to be most fruitful[1,2]. According to this method the inductive and resonance effects can be estimated from the respective σ_I and σ_R^0 constants, the latter being obtained from the ^{19}F chemical shifts of *meta*, and *para*-substituted fluorobenzenes.

The application of the Taft approach to the phenyl derivatives of Hg[3], and of Sn, Ge, Si[4] has revealed that these metals possess negligible withdrawing abilities towards π-interaction with phenyl nuclei. The number of studies concerned with transition metal phenyl derivatives is expanding continuously: thus phenyl compounds of Pt[5], Fe[6], Au[7] and Cu[8] have been investigated. Recently, Treichel and Stewart have studied in detail some fluorophenyl derivatives of Mn, Fe and Ni, using the ^{19}F NMR technique, and have submitted a systematic analysis of the experimental data on Pt derivatives[9]. All the organometallic substituents discussed in their work possess donor resonance effects. However, in going from one substituent to another, together with variation of the metal atom, of the coordinative geometry and changing the

TABLE 1

THE IR AND PMR SPECTRA OF π-CYCLOPENTADIENYL CARBONYL COMPLEXES OF MOLYBDENUM AND TUNGSTEN

No.	Complex	$\nu(CO)^a$ (cm^{-1})	PMR[b]		
			J(P–H) (Hz)	$\delta(C_5H_5)$ (ppm)	$\delta(C_6H_5)$ (ppm)
(I)	$C_5H_5W(CO)_3C_6H_4F$-*m*	1920 vs 2020 s		s 5.39	m 7.05
(II)	$C_5H_5W(CO)_3C_6H_4F$-*p*	1925 vs 2022 s		s 5.39	m 7.12
(III)	$C_5H_5W(CO)_2PPh_3C_6H_4F$-*m*	1857 s 1946 s	1.5	d 4.80	m (7.35–7.56)
(IV)	$C_5H_5W(CO)_2PPh_3C_6H_4F$-*p*	1855 vs 1944 s	1.5	d 4.75	m 7.35–7.57
(V)	$C_5H_5Mo(CO)_2PPh_3C_6H_4F$-*m*	1863 vs 1947 s	1.4	d 4.84	m 7.34–7.56
(VI)	$C_5H_5Mo(CO)_2PPh_3C_6H_4F$-*p*	1860 vs 1944 s	1.4	d 4.80	m 7.34–7.56
(VII)	$C_5H_5Mo(CO)_2PPh_3COC_6H_4F$-*p*	1864 vs 1948 s 1599 w[c]	1.4	d 5.12	m 7.34–7.54
(VIII)		1935 vs 2031 s 1674 ms[d]		s 5.48	H^α 7.41[e] H_β 7.70

[a] In $CHCl_3$; vs = very strong, s = strong, ms = medium strong, w = weak. [b] In $CDCl_3$; s = singlet; d = doublet, m = multiplet. [c] Benzoyl. [d] Acetyl. [e] $\delta(CH_3)$ 2.50.

ligands bonded to the metal, only a negligible change was observed in the measured values of σ_R^0 constants. Upon ligand replacement in a series of related compounds of the same metal, the values of σ_R^0 were practically constant. On the other hand, the σ_I constants varied over quite a wide range of values and were sensitive towards any changes in the metal atom. The authors came to the conclusion that π-interaction in the bond M–C_6H_5 is rather small in comparison to σ-interaction.

In the present work we have undertaken a ^{19}F NMR study of some *m*- and *p*-fluorophenyl complexes of Mo and W.

The complexes obtained and their yields (%) are listed in Table 3, where they are numbered as in Table 1. The following methods have been used for their syntheses:

(*A*) Action of fluoro-substituted diphenyliodonium salts on the cyclopentadienylmetal carbonyl anion:

$$C_5H_5M(CO)_n(PPh_3)_{3-n}^-Na^+ + (FC_6H_4)_2II \rightarrow C_5H_5M(CO)_n(PPh_3)_{3-n}C_6H_4F + [C_5H_5M(CO)_n(PPh_3)_{3-n}]_2 + C_5H_5M(CO)_n(PPh_3)_{3-n}I$$

Using this method, complexes (I) and (II) ($M = W$, $n = 3$) as well as (V) and (VI) ($M = Mo$, $n = 2$, $3 - n = 1$) were obtained. The yield of complex (VI) was not sufficiently high for this method of preparation to be used.

(*B*) Decarbonylation of fluorobenzoyl derivatives using $Rh(PPh_3)_3Cl$ as a decarbonylating agent:

$$C_5H_5Mo(CO)_2PPh_3COC_6H_4F + Rh(PPh_3)_3Cl \rightarrow C_5H_5Mo(CO)_2PPh_3C_6H_4F + Rh(CO)(PPh_3)_2Cl + PPh_3$$

The *p*-fluorophenyl complex (VI) was obtained in excellent yield using this method. The use of benzene instead of CH_2Cl_2 markedly increased the product yield[10].

(*C*) Complexes (III) and (IV) were prepared by reaction of PPh_3 with phenyl derivatives (I) and (II):

$$C_5H_5W(CO)_3C_6H_4F + PPh_3 \rightarrow C_5H_5W(CO)_2PPh_3C_6H_4F$$

All the complexes were characterized by elemental analysis.

Complexes (I)–(II) are yellow crystalline substances, stable in air when solids, but decomposing in solution. Their IR and PMR spectra are shown in Table 1. As seen from the data of Table 1, all the phosphine-containing complexes (III)–(VII) exhibit a doublet in the region corresponding to the cyclopentadienyl protons in their ^1H NMR spectra, with a spin–spin coupling constant of about 1.5 Hz. Two interpretations of these signals are possible:

(1). The doublet corresponds to the pure *trans*-isomer existing in solution.

(2). The doublet corresponds to an averaged spectrum with a fast *cis–trans* interconversion.

Although a preliminary choice of one of these two explanations is not possible, version (1) seems to be the most reasonable in the view of the following:

(*a*). The value J 1.4–1.5 Hz is in the vicinity of J 1.3 Hz for the pure *trans*-isomer[11] of $C_5H_5Mo(CO)_2[P(OC_6H_5)_3]CH_3$ (the *cis*-isomer has a J value of zero). In the case of an averaged spectrum the value of J should be considerably lower.

(*b*). Faller[11] has observed that in the related systems $C_5H_5Mo(CO)_2LR$ (L = phosphorus ligand, R = allyl, benzyl, etc.) fast exchange and spectrum averaging takes place at rather high temperatures (above 130°).

(*c*). All attempts to convert a possible averaged spectrum to a "stationary" one by decreasing the temperature were unsuccessful. Unfortunately the solubility of complexes (III)–(VII) is rather low even in such a good solvent as $CDCl_3$ at temperatures below 0° which hinders investigation of these complexes.

Thus the *trans*-configuration has been assigned to complexes (III)–(VII).

RESULTS AND DISCUSSION

The ^{19}F chemical shifts and the σ_R^0 and σ_I constants are presented in Table 2. As seen from the negative values of the constants, all cyclopentadienyl metal carbonyl substituents possess both donor inductive and resonance effects with respect to the phenyl ring. Compounds (I) and (II) were studied not only in chloroform but also in such coordinating solvents as tetrahydrofuran and dimethyl sulfoxide. The results obtained indicate that solvent replacement does not essentially change the ^{19}F chemical shifts or the σ_I and σ_R^0 constants. Apparently there is no coordination between the metal atom and THF and DMSO molecules for when the metal is able to coordinate with solvent molecules (as occurs with organomercury compounds[3] a substantial change in the ^{19}F chemical shifts and the σ_I constants is generally observed.

It can therefore be concluded that in complexes (I) and (II), due to the metal atom being electronically and coordinately saturated, no coordination with DMSO and THF occurs. A similar state of affairs also probably exists for the phosphine-substituted complexes (III)–(VI), but their investigation in other solvents besides $CHCl_3$, even with the use of accumulative methods, was hindered by their low solubility.

TABLE 2

^{19}F CHEMICAL SHIFTS AND σ^0_R AND σ_I CONSTANTS FOR π-CYCLOPENTADIENYL CARBONYL COMPLEXES OF MOLYBDENUM AND TUNGSTEN

Substituent	solvent	δ_m^F	δ_p^F	σ_I	σ^0_R
$C_5H_5W(CO)_3$	$CHCl_3$	1.84	7.50	−0.17	−0.19
	THF	2.05	7.95	−0.20	−0.20
	DMSO	1.88	8.02	−0.18	−0.21
$C_5H_5W(CO)_2PPh_3$	$CHCl_3$	3.70	9.5	−0.44	−0.20
$C_5H_5Mo(CO)_2PPh_3$	$CHCl_3$	3.10	9.9	−0.35	−0.23

Since for complexes (I) and (II) the values of σ_I and σ^0_R are apparently independent of the solvent, it is quite feasible to compare these constants with those tested in the data of Treichel and Stewart[9] and obtained in CH_2Cl_2.

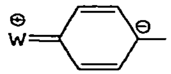
For $C_5H_5W(CO)_3$, the absolute value of σ^0_R is very much less than the respective values for $C_5H_5NiPPh_3$ (−0.30), $C_5H_5Fe(CO)_2$ (−0.29) and $Mn(CO)_5$ (−0.23). The constants σ_I differ to an even greater extent: $C_5H_5NiPPh_3$ (−0.44), $C_5H_5Fe(CO)_2$ (−0.25), $C_5H_5W(CO)_3$ (−0.17), $Mn(CO)_5$ (−0.01). The nucleophility of the respective metal carbonyl anions decreased in the same order, *i.e.*: $C_5H_5Fe(CO)_2 > C_5H_5W(CO)_3 > Mn(CO)_5$ (ref. 12).

From the data listed in Table 2 it follows that the replacement of one CO group by PPh_3 in complexes (I) and (II) results in a considerable increase in the value of σ_I (from −0.17 to −0.44; $\Delta\sigma_I$ 0.27), while σ^0_R is practically unaffected. The variation in the values of these constants is even more significant if account is taken of the fact that for ordinary organic substituents negative values of σ_I are usually found[13] in the range 0–0.12, whilst the range of negative σ^0_R values is considerably greater (from 0 to −0.54). A similar state of affairs apparently exists with $Mn(CO)_5$, $Mn(CO)_4L$ and $Mn(CO)_3L_2$ substituents (L phosphorus ligand)[9].

Thus the increase in electron density at the metal atom caused by the introduction of PPh_3 is transferred to the phenyl ring only as an increase in the inductive component, *i.e.* the inductive polarization of the $W–C_6H_5$ bond is enhanced whereas π-interaction with the phenyl ring remains unchanged. On the other hand, π-interaction in the presence of two *cis*-CO groups is greater than that for PPh_3 and the value of ν(CO) is shifted to lower frequencies.

King and Houk[14] have suggested that in compounds such as $C_5H_5M(CO)_3R$ [R = Cl, Br, I, H, CH_3, $Sn(CH_3)_3$, etc., M = Mo, W] the metal d_{z^2} and d_{xy} orbitals participate in back-π-bonding with the four ligands (three CO and R) located approximately at the vertices of a square which is the base of a tetragonal-pyramid with the metal atom at its apex. One of these orbitals interacts with two diagonal ligands while the other orbital participates in back π-bonding with two other diagonal ligands. Our results indicate that for the complexes investigated such a suggestion is not in agreement with the fact that replacement of the *trans*-CO group (with respect to phenyl) by PPh_3 in complexes (I) and (II) causes no significant change in the π-

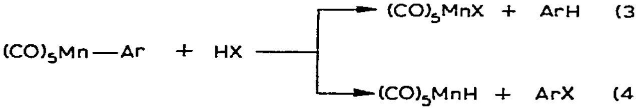
bonding and in the value of the σ_R^0 constant. If one orbital is used for π-bonding of the metal to the phenyl ring and PPh_3 then a replacement of a CO group by PPh_3 should enhance the metal ring π-bond because of the lower π-acceptor ability of PPh_3 with respect to CO. Although in the ground state some π-M–C_6H_5 bonding may occur in these complexes (owing to the occupied metal d_π orbitals and ligand antibonding π^*-orbitals), it is weak and nonspecific. The contribution of a resonance structure such as:



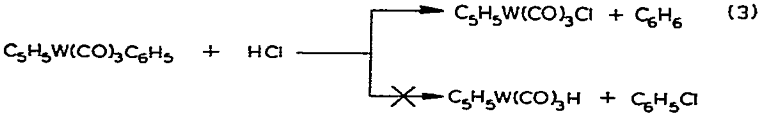
to the overall bonding is negligible.

It is therefore quite probable that in $C_5H_5W(CO)_3C_6H_5$ the W–C_6H_5 bond[15] is not noticeably shortened with respect to the sum of covalent radii (although in agreement with Treichel[9] it is probable that errors arise in determining the covalent radii of transition metals). The above resonance structure might contribute to a greater extent when the phenyl ring becomes electron-deficient, a situation which might occur upon electrophilic substitution in the benzene ring. Knox *et al.*[6] have observed an increased rate of acylation of $C_5H_5Fe(CO)_2C_6H_5$ with acetyl chloride in the presence of $AlCl_3$. We have investigated the acylation of $C_5H_5W(CO)_3C_6H_5$ with acetyl chloride in the presence of $AlCl_3$; this is complete in 10–15 min at 0°, and yields only the *p*-acetyl complex $C_5H_5W(CO)_3C_6H_4COCH_3$ (VIII). The presence of the *p*-acetyl group has been unequivocally confirmed by the appearance of a symmetric multiplet in the PMR spectrum specific to the AA'BB' system and due to the phenyl ring protons. The fact that the reaction is faster and proceeds selectively in the *para*-position may be explained in terms of the combination of the inductive donor and resonance effects of the $C_5H_5W(CO)_3$ substituent.

The inductive M–C_6H_5 σ-bond polarization is probably the main factor responsible for the polarity of the transition metal–phenyl bond. If this is so, one might expect that the value of the inductive constant should be an important factor in determining the ease of cleavage of the σ-bond in M–C_6H_5 for example by hydrogen halides (HX). It is known that in $Mn(CO)_5C_6H_5$ the Mn–C_6H_5 bond has a very low polarity (σ_I for $Mn(CO)_5$, −0.01) which might provide an explanation for two mechanisms applying for the hydrogen halide cleavage of aryl derivatives of $Mn(CO)_5$[16]:



Since σ_I is essentially more negative for $C_5H_5Fe(CO)_2$, $C_5H_5W(CO)_3$, $C_5H_5M(CO)_2$-PPh_3 (M = Mo, W), the bond polarity in such complexes should be higher and one may expect the reaction with HX to occur in accordance with route (3). Indeed $C_5H_5W(CO)_3C_6H_5$ is readily cleaved by HCl in 90% aqueous dioxane by this route, *i.e.*:



No C_6H_5Cl and $C_5H_5W(CO)_3H$ were found amongst the reaction products, $C_5H_5W(CO)_3Cl$ being produced in quantitative yield.

The fact that the unpaired electron released by the metal during two-electron M–C_6H_5 bond formation is essentially shielded by the closed electronic shell of the metal may explain the low electronegativity of the metal carbonyl substituents.

EXPERIMENTAL

IR spectra were measured on a UR-10 spectrometer. PMR spectra were recorded on a JNM-4 H-100 instrument.

^{19}F NMR spectra were measured on an R-20 Hitachi–Perkin–Elmer instrument at 56.4 MHz and 34°. Measurements were performed on diluted solutions at concentrations not greater than 0.2 mole/l. The spectra of triphenylphosphine derivatives (III)–(VI), which have low solubilities, were measured through the use of an accumulative technique. The fluorine chemical shifts were measured with respect to C_6H_5F in the same solvent by a replacement method using an electronic frequency meter. The measurements were reproducible to within ±0.1 ppm.

The data relating to elementary analyses, melting points and yields are listed in Table 3. All operations were performed under an argon atmosphere. Bis (*m*-fluorophenyl)iodonium iodide was prepared through a multi-stage process from *m*-fluoroiodobenzene using the classical method of Meyer[17]. Bis(*p*-fluorophenyl)-iodonium iodide was obtained by Beringer's method[18].

(1). *Synthesis of* $C_5H_5W(CO)_3C_6H_4F$-*m* (*I*)

A solution consisting of 5 g of $C_5H_5W(CO)_3Cl$ in 100 ml of absolute THF was stirred with a 5-fold excess of 0.8 % sodium amalgam for 1 h, the resulting solution filtered and cooled to −70° when 5.7 g of $(m-FC_6H_4)_2II$ was added with stirring. The reaction mixture was slowly heated to room temperature, stirred for 1 h, and the solvent evaporated *in vacuo*. The reaction mixture was extracted with hot heptane (3 x 100 ml) and the solution transferred to an alumina column. A yellow band was eluted with petroleum ether, 1.8 g of yellow crystals being obtained after recrystallization from heptane. In addition to iodine, subsequent elution gave $[C_5H_5W(CO)_3]_2$ (0.46 g, 11 %) and $C_5H_5W(CO)_3I$ (0.3 g, 5.1 %).

(2). *Synthesis of* $C_5H_5W(CO)_3C_6H_4F$-*p* (*II*)

Using the procedure described above, 2 g of $C_5H_5W(CO)_3C_6H_4F$-*p* were obtained from 5 g of $C_5H_5W(CO)_3Cl$ and 6 g of $(p-FC_6H_4)_2II$.

(3). *Synthesis of* $C_5H_5Mo(CO)_2PPh_3C_6H_4F$-*m* (*V*)

The procedure used for preparing this compound was exactly similar to that described earlier for $C_5H_5Mo(CO)_2PPh_3C_6H_5$[10]. $C_5H_5Mo(CO)_2PPh_3I$ (8.2 g) and 6 g of $(m\text{-}FC_6H_4)_2II$ gave 0.85 g of $C_5H_5Mo(CO)_2PPh_3C_6H_4F$-*m*, 2.32 g of $[C_5H_5Mo(CO)_2PPh_3]_2$ and 0.63 g of $C_5H_5Mo(CO)_2PPh_3I$.

(4). *Synthesis of* $C_5H_5Mo(CO)_2PPh_3C_6H_4F$-*p* (*VI*)

Using the method described in ref. 10, 9 g of $C_5H_5Mo(CO)_2PPh_3I$ and 6 g of

TABLE 3

CHARACTERISTICS OF π-CYCLOPENTADIENYL CARBONYL COMPLEXES OF MOLYBDENUM AND TUNGSTEN

Complex	Method of synth.	Yield (%)	M.p. (°C)	Analysis	
				Found	Calcd.
$C_5H_5W(CO)_3C_6H_4F$-*m*	(*A*)	33	69–70	C 39.34, 39.48	39.36
(I)				H 2.16, 2.22	2.12
$C_5H_5W(CO)_3C_6H_4F$-*p*	(*A*)	40	122–23	C 39.12, 38.98	39.36
(II)				H 2.08, 2.08	2.12
				F 4.63, 4.32	4.45
$C_5H_5W(CO)_2PPh_3C_6H_4F$-*m*	(*C*)	51	218–20	C 56.24, 56.07	56.07
(III)				H 3.56, 3.49	3.66
				P 4.58, 4.67	4.67
$C_5H_5W(CO)_2PPh_3C_6H_4F$-*p*	(*C*)	65	208–9	C 56.42	56.07
(IV)				H 3.89	3.66
				P 4.52, 4.48	4.67
$C_5H_5Mo(CO)_2PPh_3C_6H_4F$-*m*	(*A*)	12	174–75	C 64.23, 64.38	64.96
(V)			dec.	H 4.35, 4.36	4.18
				P 5.29, 5.34	5.40
$C_5H_5Mo(CO)_2PPh_3C_6H_4F$-*p*	(*A*)	4	174	C 64.42, 64.66	64.96
(VI)	(*B*)	75		H 4.01, 4.09	4.18
				P 5.14, 5.14	5.40
$C_5H_5Mo(CO)_2PPh_3COC_6H_4F$-*p*		33	142–43	C 63.18, 63.34	63.79
(VII)				H 3.82, 3.84	4.01
				P 5.32, 5.27	5.14
$C_5H_5W(CO)_3C_6H_4COCH_3$		28	129	C 42.42, 42.59	42.49
(VIII)				H 2.75, 2.71	2.65
				W 40.16, 40.43	40.69

(p-$FCH_4)_2$II gave 0.3 g of $C_5H_5Mo(CO)_2PPh_3C_6H_4F$-*p*, 2.5 g of $[C_5H_5Mo(CO)_2PPh_3]_2$ and 1.4 g of $C_5H_5Mo(CO)_2PPh_3I$.

(5). *Synthesis of $C_5H_5Mo(CO)_2PPh_3COC_6H_4F$-p (VII)*

Using a method similar to that described earlier[10], 4.2 g of $C_5H_5Mo(CO)_2PPh_3I$ and 1.1 g of p-FC_6H_4COCl afforded 1.4 g of $C_5H_5Mo(CO)_2PPh_3COC_6H_4F$-*p*.

(6). *Decarbonylation of $C_5H_5Mo(CO)_2PPh_3COC_6H_4F$-p (VII)*

(VII) (0.15 g) and 0.23 g of $ClRh(PPh_3)_3$ were stirred in benzene at 70° for 4 h. After cooling to room temperature, the solvent was evaporated *in vacuo* and the residue extracted with 10 ml of CH_2Cl_2. The insoluble yellow powder recovered was found to be $ClRh(CO)(PPh_3)_2$. The filtrate was chromatographed over alumina and the yellow band eluted with a heptane/benzene mixture (1/1). $C_5H_5Mo(CO)_2PPh_3C_6H_4F$-*p* (VI) (0.108 g) was obtained in the form of yellow crystals.

(7). *Synthesis of $C_5H_5W(CO)_2PPh_3C_6H_4F$-p (IV)*

A mixture of 2.4 g of $C_5H_5W(CO)_3C_6H_4F$-*p* and 2.94 g of PPh_3 was irradiated by means of a PRK-4 UV lamp with magnetic stirring at 25° for 16 h. The yellow suspension was filtered, the benzene evaporated *in vacuo*, and the residue extracted with a hot benzene/petroleum ether mixture (1/1) and the extract chromatographed on an alumina column using the same solvent mixture as an eluant. PPh_3, 0.4 g of $C_5H_5W(CO)_3C_6H_4F$-*p* (II) and 2.42 g of $C_5H_5W(CO)_2PPh_3C_6H_4F$-*p* (IV) were obtained in order of elution. The product was recrystallized from a CH_2Cl_2/methanol mixture (1/1).

(8). *Synthesis of* $C_5H_5W(CO)_2PPh_3C_6H_4F$-*m* (*III*)

Using the procedure described above, 0.68 g of $C_5H_5W(CO)_2PPh_3C_6H_4F$-*m* was obtained from 0.86 g of $C_5H_5W(CO)_3C_6H_4F$-*m* and 1.07 g of PPh_3 after 15 h of irradiation.

(9). *Cleavage of* $C_5H_5W(CO)_3C_6H_5$ *with hydrogen chloride*

$C_5H_5W(CO)_3C_6H_5$ (0.1 g) was dissolved in 6.5 ml of 90% aqueous dioxane containing an equimolar amount of HCl. After 12 h at room temperature the solution became red. The mixture was allowed to stand for two days, when chromatographic separation gave 0.08 g of $C_5H_5W(CO)_3Cl$.

(10). *Acylation of* $C_5H_5W(CO)_3C_6H_5$

A mixture of 0.19 g of acetyl chloride with an equivalent amount of $AlCl_3$ was added to a solution of 1 g of $C_5H_5W(CO)_3C_6H_5$ in 50 ml of CH_2Cl_2 at 0° with vigorous stirring. The reaction mixture was stirred for 15 min at a temperature below 0° and mixed with ice-water. The organic layer was separated from the aqueous one in a separating funnel, shaken with $CaCl_2$ and the solvent removed *in vacuo*. The residue was chromatographed on an alumina column using a benzene/petroleum ether mixture (1/1) as an eluant; 0.22 g of $C_5H_5W(CO)_3Cl$ and 0.30 g of $C_5H_5W(CO)_3C_6H_4COCH_3$-*p* (VIII) were obtained in order of elution. Yellow crystals of (VIII) were recrystallized using a CH_2Cl_2/heptane mixture as a solvent.

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