# Synthesis and Properties of Tungsten(0) Carbonyl Complexes with Carbonyl-stabilized Ylides

ISAO KAWAFUNE and GEN-ETSU MATSUBAYASHI*

*Department of Applied Chemistry, Faculty of Engineering, Osaka University, Yamadaoka, Suita, Osaka 565, Japan*

Received September 27, 1982

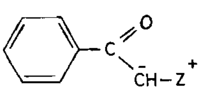
*The reactions of dimethylsulfonium, triphenylphosphonium, and 4-methylpyridinium phenacylides* ($PhC(O)\bar{C}H\overset{+}{Z}$; $\overset{+}{Z} = \overset{+}{S}Me_2$ ($Y_{Ph-S}$), $\overset{+}{P}Ph_3$ ($Y_{Ph-P}$), *and* $\overset{+}{N}C_5H_4Me\text{-}4$ ($Y_{Ph-N}$)) *with* $W(CO)_5THF$ *gave* $W(CO)_5(PhC(O)\bar{C}H\overset{+}{Z})$. *IR and* $^1H$ *NMR spectra have indicated the ylide carbon-to-tungsten linkage in* $W(CO)_5Y_{Ph-S}$ *and the coordination of the carbonyl oxygen atom in* $W(CO)_5Y_{Ph-P}$ *and* $W(CO)_5Y_{Ph-N}$. *The corresponding three 2-pyridylcarbonylmethylides* ($C_5H_4NC(O)\bar{C}H\overset{+}{Z}$; $\overset{+}{Z} = \overset{+}{S}Me_2$ ($Y_{Py-S}$), $\overset{+}{P}Ph_3$ ($Y_{Py-P}$), *and* $\overset{+}{N}C_5H_4Me\text{-}4$ ($Y_{Py-N}$)) *reacted with* $W(CO)_6$ *under UV irradiation or with* $W(CO)_5THF$ *to afford* $W(CO)_4(C_5H_4NC(O)\bar{C}H\overset{+}{Z})$. $W(CO)_4Y_{Py-S}$ *(red form),* $W(CO)_4Y_{Py-P}$, *and* $W(CO)_4Y_{Py-N}$ *have been suggested to involve the chelation through carbonyl oxygen and pyridine nitrogen on the basis of IR and* $^1H$ *NMR spectra. Another geometrical isomer of* $W(CO)_4Y_{Py-S}$ *isolated as a brown form showed the same spectral behaviors as the red complex in solution. Configurations and properties of the complexes have been discussed on the basis of IR and* $^1H$ *NMR, together with electronic absorption and emission spectra.*

## Introduction

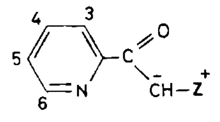
Negatively charged ylide carbon has an ability to coordinate to metal ions, and many ylide–metal complexes which contain ylide carbon–metal bonds have been prepared [1]. Ylides stabilized by a carbonyl group adjacent to a ylide carbon atom can also interact with metal ions, through the carbonyl oxygen atom. In fact, triphenylphosphoranylideneacetone is known to coordinate to chlorotrimethyltin(IV) through the carbonyl oxygen [2], while dimethylsulfonium phenacylide and dimethylsulfonium 2-pyridylcarbonylmethylide form the palladium(II) and platinum(II) complexes involving the ylide carbon-to-metal bond [3–5].

Although several ylide–tungsten(0) complexes containing the ylide carbon-to-metal bond have been prepared [6–10], no bonding scheme of carbonyl-stabilized ylides to a tungsten(0) moiety is known.

This paper reports the preparations of tungsten(0) carbonyl complexes with dimethylsulfonium, triphenylphosphonium, and 4-methylpyridinium phenacylides (*I*), and the corresponding 2-pyridylcarbonylmethylides (*II*). The configurations and properties of these complexes are discussed on the basis of $^1H$ NMR, IR, and electronic absorption and emission spectra.



(I)



(II)

$\overset{+}{Z} = \overset{+}{S}Me$, $\overset{+}{P}Ph_3$, and $\overset{+}{N}C_5H_4Me\text{-}4$

## Experimental

### *Dimethylsulfonium 2-Pyridylcarbonylmethylide,* $C_5H_4NC(O)\bar{C}H\overset{+}{S}Me_2$ ($Y_{Py-S}$)

A solution containing 2-(bromoacetyl)pyridine [11] (2.5 g, 12 mmol) and dimethylsulfide (1.6 g, 25 mmol) in methanol (25 cm$^3$) was stirred for 3 h at room temperature, and evaporated to dryness under reduced pressure. The resulting product was dissolved in water (10 cm$^3$), followed by addition of a 4 mol dm$^{-3}$ NaOH aqueous solution (10 cm$^3$). After stirring for 0.5 h the solution was shaken with dichloromethane (20 cm$^3$) several times. The dichloromethane layer was evaporated to dryness. The product was recrystallized from a mixture of dichloromethane and petroleum ether to give white hygroscopic needles (0.57 g, 25% yield). M.p. 51–52 °C. *Anal.* Found: C, 59.67; H, 5.94; N, 7.65%. $C_9H_{11}NOS$ Calcd.: C, 59.64; H, 6.12, N, 7.73%.

---

*Author to whom all correspondence should be addressed.

0020-1693/83/0000-0000/$03.00

### *Triphenylphosphonium 2-Pyridylcarbonylmethylide, $C_5H_4NC(O)\bar{C}H\overset{+}{P}Ph_3$ ($Y_{Py-P}$)*

A chloroform solution (10 $cm^3$) of triphenylphosphine (0.69 g, 2.6 mmol) was added to 2-(bromoacetyl)pyridine (0.53 g, 2.6 mmol) in chloroform (10 $cm^3$). After being stirred for 20 h at room temperature, the solution was evaporated to dryness under reduced pressure to afford an oily material, to which diethyl ether (30 $cm^3$) was added and stirred, giving a precipitate. This was collected by filtration, and dissolved in a 1 mol $dm^{-3}$ NaOH aqueous solution (80 $cm^3$). The solution was refluxed for 2 h to separate out a rubberlike solid, which was filtered and recrystallized from a mixture of dichloromethane and petroleum ether, giving colorless cubic crystals (0.42 g, 42% yield). M.p. 129–133 °C. *Anal.* Found: C, 75.15; H, 5.41; N, 3.43%. $C_{25}H_{20}NOP \cdot H_2O$ Calcd.: C, 75.17; H, 5.55; N, 3.51%.

### *Other Ylides*

4-Methylpyridinium 2-pyridylcarbonylmethylide ($Y_{Py-N}$) [5], 4-methylpyridinium phenacylide ($Y_{Ph-N}$) [12], dimethylsulfonium phenacylide ($Y_{Ph-S}$) [13], and triphenylphosphonium phenacylide ($Y_{Ph-P}$) [14] were prepared according to literature methods.

### *Phenacylide–Tungsten(0) Complexes*

To $W(CO)_5THF$ prepared by the UV irradiation of $W(CO)_6$ (0.50 g, 1.4 mmol) in THF (70 $cm^3$) [15] was added a THF solution (20 $cm^3$) of $Y_{Ph-S}$ (0.23 g, 1.3 mmol) at 5–10 °C. After being stirred for 2 h below 10 °C, the solution was concentrated to about a half volume under reduced pressure, followed by addition of petroleum ether (40 $cm^3$). The solution was allowed to stand at about 5 °C overnight to give a yellow precipitate of $W(CO)_5Y_{Ph-S}$, which was collected by filtration and dried *in vacuo* (0.43 g, 60% yield). M.p. 66–70 °C. *Anal.* Found: C, 35.36; H, 2.30%. $C_{15}H_{12}O_6SW$ Calcd.: C, 35.74; H, 2.40%. $W(CO)_5THF$ photo-generated from $W(CO)_6$ (0.50 g, 1.4 mmol) reacted similarly with $Y_{Ph-P}$ (0.49 g, 1.3 mmol) and $Y_{Ph-N}$ (0.27 g, 1.3 mmol) to afford a yellow precipitate of $W(CO)_5Y_{Ph-P}$ (0.31 g, 50% yield) and a brown precipitate of $W(CO)_5Y_{Ph-N}$ (0.42 g, 60% yield) respectively. $W(CO)_5Y_{Ph-P}$, M.p. 122–125 °C. *Anal.* Found: C, 53.02; H, 3.21%. $C_{31}H_{21}O_6PW$ Calcd.: C, 52.86; H, 3.01%. $W(CO)_5Y_{Ph-N}$, M.p. >95 °C (decomp.). Found: C, 42.71; H, 2.73; N, 2.70%. $C_{19}H_{13}NO_6W$ Calcd.: C, 42.64; H, 2.45; N, 2.62%.

### *2-Pyridylcarbonylmethylide–Tungsten(0) Complexes*

$W(CO)_5THF$ obtained from $W(CO)_6$ (0.5 g, 1.4 mmol) reacted with $Y_{Py-S}$ (0.24 g, 1.3 mmol) in THF at 5–10 °C to yield red crystals of $W(CO)_4Y_{Py-S}$ (0.31 g, 50% yield). M.p. >300 °C. *Anal.* Found: C, 32.65; H, 2.27; N, 3.01%. $C_{13}H_{11}NOSW$ Calcd.: C, 32.72; H, 2.32; N, 2.94%. A brown complex with the same composition was isolated as a benzene solvate by the reaction of $W(CO)_6$ (0.33 g, 0.9 mmol) with $Y_{Py-S}$ (0.21 g, 1.1 mmol) in benzene (70 $cm^3$); the reactant solution was irradiated by UV light at room temperature for 5 h, during which time the evolution of CO ceased and a brown precipitate of $W(CO)_4Y_{Py-S}$ separated out. The precipitate was collected by filtration, washed with benzene, and dried *in vacuo* (0.29 g, 56% yield). M.p. >140 °C (decomp.). *Anal.* Found: C, 36.70; H, 2.55; N, 3.10%. $C_{13}H_{11}NOSW \cdot 1/2C_6H_6$ Calcd.: C, 37.22; H, 2.73; N, 2.71%. The UV irradiation on a mixture of $W(CO)_6$ (0.33 g, 0.9 mmol) with $Y_{Py-P}$ (0.42 g, 1.1 mmol) or $Y_{Py-N}$ (0.23 g, 1.1 mmol) in benzene (70 $cm^3$) similarly afforded a brown precipitate of $W(CO)_4Y_{Py-P}$ (0.33 g, 50% yield) or a violet precipitate of $W(CO)_4Y_{Py-N}$ (0.29 g, 60% yield). $W(CO)_4Y_{Py-P}$, M.p. >115 °C (decomp.). *Anal.* Found: C, 54.49; H, 3.26; N, 1.89%. $C_{29}H_{20}NO_5PW \cdot 2/3C_6H_6$ Calcd.: C, 53.93; H, 3.32; N, 1.92%. $W(CO)_4Y_{Py-N}$, M.p. >240 °C (decomp.). Found: C, 40.12; H, 2.30; N, 5.44%. $C_{17}H_{12}N_2O_5W$ Calcd.: C, 40.18; H, 2.38; N, 5.51%.

### *Spectra*

Electronic and IR absorption spectra were recorded on Hitachi 124 and 215 spectrophotometers respectively. $^1H$ NMR spectra were measured with a JEOL JNM-PS-100 spectrometer (operating at 100 MHz at 24 °C), using TMS as the internal standard. Emission spectra were measured with a Hitachi MPF-3 spectrophotometer. All the spectral measurements were carried out for the complexes dissolved in degassed or nitrogen gas-purged solvents, because the complexes are oxygen-sensitive in solution.

## Results and Discussion

### *Configurations of the Ylide–Tungsten(0) Complexes*

The $^1H$ NMR spectrum of $W(CO)_5Y_{Ph-S}$ in acetone-$d_6$ showed the ylide methine proton ($H_a$) signal at 6.69 $\delta$ accompanied with satellites due to spin–spin coupling with the $^{183}W$ nucleus ($^2J(^{183}W-H_a) = 5.1$ Hz), which confirms the coordination of $Y_{Ph-S}$ to tungsten through the ylide carbon atom. The coordination of the ylide carbon is compatible with the appearance of two S-methyl proton signals (3.19 and 2.89 $\delta$) owing to asymmetry of the ylide carbon. Such a coordination mode is also supported by the fact that the IR $\nu(C{=}O)$ band occurred at a higher frequency than that of the free ylide (Table I) [3]. On the other hand, no spin–spin coupling between the $^{183}W$ nucleus and the ylide methine proton has been noticed in the $^1H$ NMR spectrum of $W(CO)_5Y_{Ph-P}$ in acetone-$d_6$. Moreover, the coupling constant between the $^{31}P$ nucleus and the ylide

TABLE I. Relevant IR Frequencies (cm$^{-1}$) of W(CO)$_5$Y$_{Ph-Z}$ in THF.

| $Y_{Ph-Z}$ | $\nu$(C≡O) | | | | $\nu$(C=O)$^a$ |
|---|---|---|---|---|---|
| | A$_1$(2) | B$_1$ | E | A$_1$(1) | |
| $Y_{Ph-S}$ | 2060 | 1968 | 1923 | 1897 | 1617 (86) |
| $Y_{Ph-P}$ | 2066 | 1972 | 1918 | 1862 | 1490 (−36) |
| $Y_{Ph-N}$ | 2059 | 1973 | 1916 | 1861 | 1536 (14) |

$^a\nu_{complexed} - \nu_{free}$ in parentheses.

methine proton of the complex (24.0 Hz) was very close to that of the free ylide (25.5 Hz). This is in contrast with a small coupling constant (5.9 Hz) in Pd$^{II}$Cl(Bu$^t_2$NO)Y$_{Ph-P}$, having a ylide carbon–palladium bond [16]. These findings suggest the coordination of Y$_{Ph-P}$ to tungsten through the carbonyl oxygen atom. This is compatible with the fact that the $\nu$(C=O) band of the complex did not appear above 1500 cm$^{-1}$ in the solid state and in THF. The coordination via the carbonyl oxygen atom is also suggested for W(CO)$_5$Y$_{Ph-N}$.

The three phenacylide complexes display four $\nu$(C≡O) bands which are analogous to the spectra of W(CO)$_5$L (L = amines, sulfides and tertiary phosphines ) [17, 18]. These $\nu$(C≡O) frequencies are 10–50 cm$^{-1}$ lower than those of W(CO)$_5$L, suggesting that both the ylide carbon and carbonyl oxygen atoms of the phenacylides coordinate to the W(CO)$_5$ moiety as a weaker $\pi$-acceptor than sulfides and tertiary phosphines, and as a somewhat stronger $\sigma$-donor than amines.

Two isomers of W(CO)$_4$Y$_{Py-S}$ were isolated: red and brown. The red complex in THF exhibited the $\nu$(C=O) band at 6 cm$^{-1}$ lower frequency than that of free Y$_{Py-S}$. The $^1$H NMR spectrum of the complex in THF gave an S-methyl proton signal (2.99 $\delta$). These findings are in contrast with the facts that the coordination through the ylide carbon results in a higher frequency shift of the $\nu$(C=O) vibration and the appearance of two S-methyl proton signals, as seen in W(CO)$_5$Y$_{Ph-S}$ and PtCl$_2$Y$_{Py-S}$ [4]. Thus, the present complex seems to assume the coordination through the carbonyl oxygen atom in this solvent. The coordination through the pyridyl nitrogen is supported by the fact that the H$_6$ signal occurred at a considerably low field compared with that of free ylide. The chelation of Y$_{Py-S}$ to tungsten through the carbonyl oxygen and pyridyl nitrogen atoms is compatible with an X-ray crystallographic analysis for the red form complex of W(CO)$_4$Y$_{Py-S}$ [19].

On the other hand, the $\nu$(C=O) band of the complex in DMSO was observed at 9 cm$^{-1}$ higher frequency than that of free ylide (Table II). Furthermore, in THF–DMSO mixtures the complex displayed two $\nu$(C=O) bands, whose relative intensities varied with the ratios of the two solvents (Fig. 1). The configuration of W(CO)$_4$Y$_{Py-S}$ in DMSO would

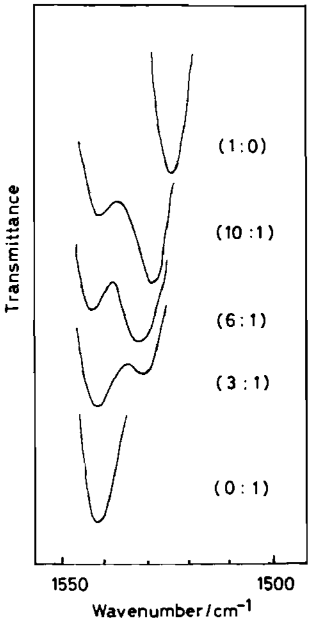


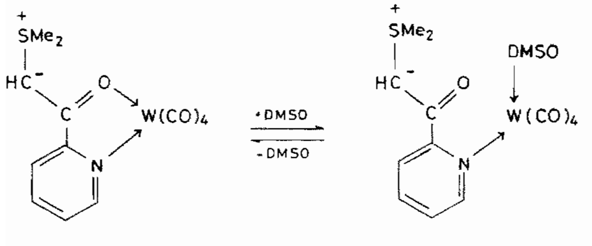
Fig. 1. The $\nu$(C=O) bonds of W(CO)$_4$Y$_{Py-S}$ in THF–DMSO mixtures; the volume ratios (THF:DMSO) in parentheses.

TABLE II. Relevant IR Frequencies (cm$^{-1}$) and $^1$H NMR Chemical Shifts of H$_6$ Signals for W(CO)$_4$Y$_{Py-Z}$.

| $Y_{Py-Z}$ | Medium | $\nu$(C≡O) | | | | $\nu$(C=O)$^a$ | $\delta$ H$_6$$^b$ |
|---|---|---|---|---|---|---|---|
| $Y_{Py-S}$ (red form) | Nujol | 2002 | 1897 | 1845 | 1781 | 1524 (5) | |
| $Y_{Py-S}$ (brown form) | Nujol | 1995 | 1865 | 1828 | 1780 | 1540 (21) | |
| $Y_{Py-S}$$^c$ | THF | 1998 | 1873 | 1858 | 1813 | 1526 (−6) | 9.06 (0.67) |
| | DMSO | 1993 | 1860 | 1846 | 1799 | 1542 (9) | 8.93 (0.48) |
| $Y_{Py-P}$ | Nujol | 1994 | 1875 | 1841 | 1782 | 1514 (3) | |
| | THF | 1997 | 1868 | 1860 | 1814 | 1513 (−9) | 9.00 (0.54) |
| | DMSO | 1997 | 1866 | 1848 | 1799 | 1525 (−1) | 8.91 (0.41) |
| $Y_{Py-N}$$^d$ | Nujol | 1999 | 1899 | 1839 | 1761 | 1502 (−26) | |
| | DMSO | 1993 | 1858 | 1843 | 1797 | 1502 (−24) | 9.07 (0.61) |

$^a\nu_{complexed} - \nu_{free}$ in parentheses. $^b\delta_{complexed} - \delta_{free}$ in parentheses. $^c$Both the red and brown form complexes exhibited the identical spectra in the solutions. $^d$Too insoluble in THF for the measurement.

therefore be different from that in THF. Although two $\nu$(C=O) bands due to the two species were observed in THF–DMSO mixtures, no separated $^1$H NMR signals of the coordinating ylides appeared. Furthermore, all the signals were not varied by the addition of free $Y_{Py-S}$. These findings indicate a fast interconversion between the two species on the NMR time-scale. Coordination to tungsten through the ylide carbon is implausible in DMSO, since the high frequency shift of the $\nu$(C=O) band upon complexation is too small and the $^1$H NMR spectrum of the complex showed only an S-methyl signal. The $H_6$ signal occurred at a fairly low field compared with that of free ylide, which indicates the coordination through pyridine nitrogen. Thus, assuming a hexacoordinated tungsten moiety in DMSO, the species (*III*) proposed in THF seems to change to the species (*IV*), in which both nitrogen and a DMSO molecule coordinate to tungsten, but the carbonyl oxygen and ylide carbon atoms do not participate in the coordination. This may be ascribed to a strong coordination ability of DMSO to metal ions [20]. Although the configuration of the brown isomer in the solid state has not been determined in the present paper, its IR and $^1$H NMR spectra in THF or in DMSO are identical with those of the red form complex.



(III) (IV)

$W(CO)_4Y_{Py-P}$ is likely to have a similar configuration around tungsten to $W(CO)_4Y_{Py-S}$, since their behaviors in $^1$H NMR and IR spectra have been essentially the same. The $\nu$(C=O) band of $W(CO)_4Y_{Py-N}$ in the solid state and in DMSO was observed at a lower frequency than that of the free ylide, suggesting that $Y_{Py-N}$ is linked to tungsten through the carbonyl oxygen atom in both the states.

### *Electronic Absorption and Emission Spectra of the Complexes*

Figure 2 shows the electronic absorption spectrum of $W(CO)_5Y_{Ph-S}$ in 2-MeTHF. The absorption bands in the region of 300–450 nm were almost unchanged in DMSO at room temperature, and also in 2-MeTHF at 77 K. Since tungsten-to-ligand charge transfer bands observed for several $W(CO)_5L$ (L = pyridine and its derivatives) were reported to depend significantly on solvents and temperature in the measurements [21], the bands at 368 and 418 nm in the present complex are not likely to be due to tungsten-to-ligand charge transfer transition, but tentatively assigned to $^1$A–$^1$E and $^1$A–$^3$E ligand field d–d transitions, respectively, as reported in several $W(CO)_5L'$ (L′ = amines) [22]. Furthermore, the band at 336 nm is reasonably assigned to a transition from tungsten to $\pi^*$(C≡O) [23].

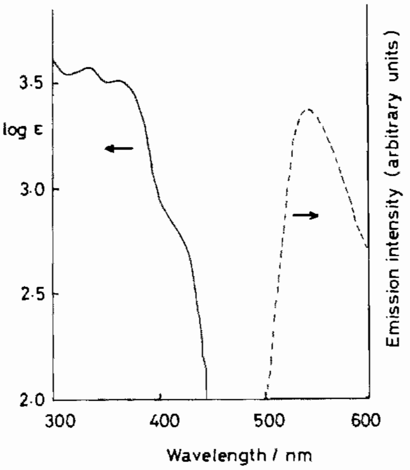


Fig. 2. Absorption (——) and emission spectra (– – –) of $W(CO)_5Y_{Ph-S}$ in 2-MeTHF at 298 and 77 K respectively.

TABLE III. Absorption (at 298 K) and Emission (at 77 K) Maxima (nm) for $W(CO)_5$- and $W(CO)_4Y_{Py-Z}$ in 2-MeTHF.

| Complex | Absorption (logε) | | | | Emission [a] |
|---|---|---|---|---|---|
| | W → π* (C≡O) | $^1A_1 \rightarrow {}^1E$ | $^1A_1 \rightarrow {}^3E$ | (W → $Y_{Py-Z}$)CT | $^3E \rightarrow {}^1A_1$ |
| $W(CO)_5Y_{Ph-S}$ | 336 (3.6) | 368 (3.5) | 418 sh | | 540 (420) |
| $W(CO)_5Y_{Ph-P}$ | 333 (4.0) | 418 (3.7) | 464 sh | | 515 (454) |
| $W(CO)_5Y_{Ph-N}$ | b | b | b | | d |
| $W(CO)_4Y_{Py-S}$ | 310 (4.3) | 411 sh | | 467 (3.7) | Not observed |
| $W(CO)_4Y_{Py-P}$ | 312 (4.3) | 430 sh | | 486 (3.9) | Not observed |
| $W(CO)_4Y_{Py-N}$ | 310 (4.0) | c | | 558 (4.0) | Not observed |

[a] Exciting wavelengths (nm) maximizing the emission intensities in parentheses. [b] A broad band was observed at 427 nm (logε = 4.2). [c] The ligand field d–d bands were obscured by the intraligand charge transfer band (367 nm, logε = 4.22) and the CT(W $Y_{Py-N}$) one. [d] Although a weak emission was observed at 483 nm (excitation maximum, 440 nm), the emission may be due to the intraligand charge transfer transition.

$W(CO)_5Y_{Ph-S}$ exhibited a weak emission in 2-MeTHF at 77 K (Fig. 2), although no emission was observed for the complex at room temperature and for free $Y_{Ph-S}$ even at 77 K. The excitation wavelength (420 nm) which maximized the emission intensity essentially agreed with the wavelength of $^1A$–$^3E$ transition band at 77 K. Thus, the observed emission seems to be ascribed to the $^3E$–$^1A$ transition, as reported in many $W(CO)_5L'$ complexes ($L'$ = amines) [21]. Similar absorption and emission spectra were observed for $W(CO)_5Y_{Ph-P}$. On the other hand $W(CO)_5Y_{Ph-N}$ showed an intense absorption band at 427 nm ($\log\epsilon = 4.2$) in 2-MeTHF, which may obscure the ligand field d–d bands (Table III). This intense band is reasonably assigned to a transition due to the charge transfer between the ylide carbon and pyridinium nitrogen atoms, which was observed in the absorption spectrum of $Y_{Ph-N}$ in the same solvent (451 nm, $\log\epsilon = 4.0$). The occurrence of this band for the metal complex indicates a preserved planar $sp^2$ configuration around the ylide carbon atom which resulted from the coordination through the carbonyl oxygen atom.

In the absorption spectra of $W(CO)_4Y_{Py-S}$ in 2-MeTHF the band observed at the longest wavelength at room temperature showed a blue shift at 77 K (Fig. 3). In addition, the band occurred at a higher frequency in acetonitrile than in 2-MeTHF. Thus, this band is reasonably assigned to tungsten-to-ylide charge transfer transition, in view of the similar temperature and solvent dependences of tungsten-to-ligand charge transfer bands of some $W(CO)_4L$–$L$ complexes (L–L = 1,10-phenanthroline [24] and diazabutadiene [25]). The longest wavelength bands of $W(CO)_4Y_{Py-P}$ and $W(CO)_4Y_{Py-N}$ also exhibited a similar spectral behavior to that of $W(CO)_4Y_{Py-S}$. $W(CO)_4Y_{Py-Z}$ (Z = S, P and N) exhibited no emission in 2-MeTHF or in MeOH/EtOH (1:4 V/V), even at 77 K.

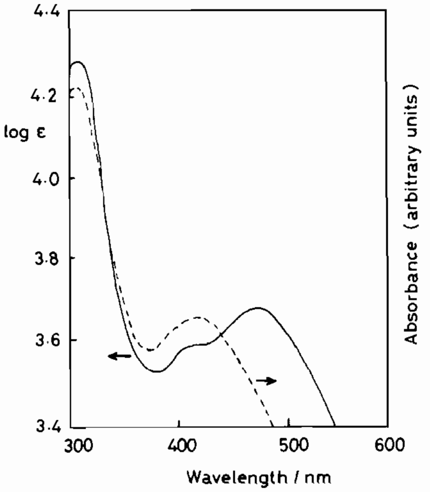


Fig. 3. Electronic absorption spectra of $W(CO)_4Y_{Py-S}$ in 2-MeTHF at room temperature (——) and 77 K (– – –).

## Acknowledgment

We thank Professor Toshio Tanaka for his continuous encouragement throughout this study.

## References

1 H. Schmidbaur, *Acc. Chem. Res., 8,* 62 (1975).
2 J. Buckle, P. G. Harrison, T. J. King and J. A. Richards, *Chem. Comm.,* 1104 (1972); *J. Chem. Soc. Dalton,* 1552 (1975).
3 H. Koezuka, G. Matsubayashi and T. Tanaka, *Inorg. Chem., 13,* 433 (1974); *15,* 417 (1976).
4 G. Matsubayashi, Y. Kondo, T. Tanaka, S. Nishigaki and K. Nakatsu, *Chem. Lett.,* 375 (1979).
5 G. Matsubayashi and Y. Kondo, *J. Organometal. Chem.,* 219, 269 (1981).
6 K. A. O. Starzewski, H. T. Dieck, K. D. Franz and F. Hohmann, *J. Organometal. Chem., 42,* C35 (1972).
7 L. Weber, *J. Organometal. Chem., 142,* 309 (1977).
8 L. Weber, *Z. Naturforsch., 31b,* 780 (1976).
9 K. A. O. Starzewski and H. T. Dieck, *Inorg. Chem., 18,* 3308 (1979).
10 F. R. Kreissl and W. Held, *Chem. Ber., 110,* 799 (1977).
11 G. R. Clemo, W. McG. Morgan and R. Rapper, *J. Chem. Soc.,* 965 (1937).
12 F. Krohnke, *Chem. Ber., 68,* 1177 (1935).
13 K. W. Ratts and A. N. Yao, *J. Org. Chem., 31,* 1185 (1966).
14 F. Ramirez and S. Dershowitz, *J. Org. Chem., 22,* 41 (1957).
15 W. Strohmeier, *Angew. Chem., 76,* 873 (1964).
16 M. Okunaka, G. Matsubayashi and T. Tanaka, *Inorg. Nucl. Chem. Lett., 12,* 813 (1976).
17 F. A. Cotton and C. S. Kraihanzel, *J. Am. Chem. Soc., 84,* 4432 (1962); *Inorg. Chem., 2,* 533 (1963).
18 E. W. Ainscough, E. J. Birch and A. M. Brodie, *Inorg. Chim. Acta, 20,* 187 (1976).
19 G. Matsubayashi, I. Kawafune, T. Tanaka, S. Nishigaki and K. Nakatsu, *J. Organometal. Chem., 187,* 113 (1980).
20 V. Gutmann, 'Coordination Chemistry in Non-Aqueous Solutions', Springer-Verlag, New York, 19 (1968).
21 M. S. Wrighton, H. B. Abrahamson and D. L. Morse, *J. Am. Chem. Soc., 98,* 4105 (1976).
22 M. Wrighton, *Chem. Rev., 74,* 401 (1974).
23 H. Saito, J. Fujita and K. Saito, *Bull. Chem. Soc. Jpn., 41,* 359, 863 (1968).
24 M. S. Wrighton and D. L. Morse, *J. Organometal. Chem., 97,* 405 (1975).
25 L. H. Staal, A. Terpstra and D. J. Stufkens, *Inorg. Chim. Acta, 34,* 97 (1979).