

This article was downloaded by:

On: 24 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

Polymeric Metallocarbenes

Li-Ban Chen^a; Jian Lin^a; Jing-Xiu Jin^a; Gui-Chang Huang^a; Xue-Yi Li^a; Hai-Sheng Chen^a; Xin-Xin Lin^a

^a Guangzhou Institute of Chemistry Academia Sinica, Guangzhou, China

To cite this Article Chen, Li-Ban , Lin, Jian , Jin, Jing-Xiu , Huang, Gui-Chang , Li, Xue-Yi , Chen, Hai-Sheng and Lin, Xin-Xin(1989) 'Polymeric Metallocarbenes', Journal of Macromolecular Science, Part A, 26: 2, 361 – 371

To link to this Article: DOI: 10.1080/00222338908051979

URL: <http://dx.doi.org/10.1080/00222338908051979>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

POLYMERIC METALLOCARBENES

LI-BAN CHEN,* JIAN LIN, JING-XIU JIN, GUI-CHANG HUANG,
XUE-YI LI, HAI-SHENG CHEN, and XIN-XIN LIN

Guangzhou Institute of Chemistry
Academia Sinica
P.O. Box 1122, Guangzhou 510650, China

ABSTRACT

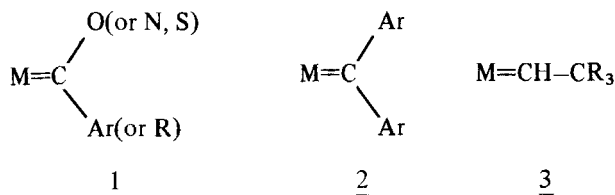
Three types of polymeric metallocarbenes were synthesized: heterocarbene, diarylcarbene, and alkylidene complexes. They were thermally more stable than their low molecular weight analogs. They exhibited ^{13}C -NMR signals for the carbene carbons at very low magnetic field. They were characterized by typical metallocarbene reactions, such as nucleophilic substitution and oxidation, as well as cyclopropanation of unsaturated carboxylates. Thus, metallocarbenes, as an important category of organometallic compounds or intermediates, have gained entry to polymer chemistry.

INTRODUCTION

Among the four main categories of active intermediates in organic reactions, carbanions, carbocations, and free radicals have been extensively studied in polymeric forms, while carbenes and their transition metal complexes have not yet been used in polymeric form. In recent decades, polymers have been widely employed as carriers of reagents or catalysts to improve their activity, selectivity, stability, and ease of recovery [1, 2]. Transition-metal carbene complexes have been found effective as reagents or catalysts in organic reactions, such as olefin metathesis or cyclopropanation, alkyne metathesis or polymerization, ketone hydrosilylation, or the Wittig reaction [3-5]. It is most desir-

able to find out whether and how the properties of a metallocarbene would be influenced by binding to a polymer carrier. For this purpose, the first task to accomplish is the synthesis of polymeric metallocarbenes.

Depending on the type of groups attached to the carbene carbons, low-molecular-weight metallocarbenes are known to be either heterocarbene 1, diarylcarbene 2, or alkylidene complexes 3 [6-8]. We have now developed the synthesis of the three analogous types of polymeric carbene complexes.



EXPERIMENTAL

IR spectra (KBr disks) were recorded with a Perkin-Elmer 325 spectrometer. ^{13}C -NMR spectra in THF or HMPT solutions were recorded with a JEOL FX-90Q spectrometer. Chemical shifts are reported in ppm relative to SiMe_4 , referenced to solvents used (the data in parentheses are the somewhat obscure bands in the spectra). Differential thermogravimetry was carried out with a Shimadzu DT-30 meter.

Solvents such as tetrahydrofuran (THF), hexamethylphosphoric triamide (HMPT), ether, cyclohexane, and petroleum ether were dried before use in the usual manner. Tetramethylethylenediamine (TMEDA), $\text{Mo}(\text{CO})_6$, and $\text{W}(\text{CO})_6$ were commercial products and were dried before use. $\text{MeLi}/\text{Et}_2\text{O}$ was also obtained commercially. $\text{PhLi}/\text{Et}_2\text{O}$, butyllithium in petroleum ether, cyclopentadienyl sodium (CpNa) [16], triethyloxonium fluoroborate (Et_3OBF_4) [13], WOCl_4 [17], and $\text{PhN}=\text{WCl}_4 \cdot \text{Et}_2\text{O}$ [8] were prepared according to the usual procedures. Neophyl chloride (NepCl) was prepared by the Friedel-Crafts reaction of methallyl chloride with benzene [14]; ^{13}C NMR (in CDCl_3): δ 145.8 (Ph, ipso), 128.0, 126.2, 125.6 (Ph), 56.0 (CH_2), 39.4 (CMe_2), 26.2 (Me). $\text{Ph}-\text{CMe}_2\text{CH}_2\text{MgCl}$ (NepMgCl) was prepared from NepCl and Mg in THF: ^{13}C NMR (in THF): δ 157.8 (Ph, ipso), 128.0, 127.3, 125.1 (Ph), 39.2 (CH_2), 35.7 (CMe_2), 31.3 (Me).

Polymer Carriers and Their Functionalization

Linear polystyrene (PS, MW 2×10^5) was commercially obtained and purified by precipitation with water from its acetone solution. Linear polystyrene

(PS, MW 8000) was prepared by radical polymerization of styrene in carbon tetrachloride solution. Copolymer beads of PS-DVB were prepared from styrene and 2 wt% of divinylbenzene [2]. Poly(tetrahydrofuran-*co*-epichlorohydrin) (P(THF-*co*-ECH), MW 4000) was prepared by the polymerization of THF and ECH in a molar ratio of 2:1 in the presence of $\text{BF}_3 \cdot \text{Et}_2\text{O}$.

Direct lithiation of polystyrene to prepare 4 was carried out in a manner similar to Farrall [9]. (Polystyryl)bipyridine, 5, was prepared according to Card et al. [10]. The cyclopentadienyl-containing polymer 6 was prepared according to Asai [11] and Grubbs [12].

Synthesis of Polymeric Heterocarbene Complexes 7a-c

A mixture of THF, 4, and an equivalent amount of $\text{M}(\text{CO})_6$ ($\text{M} = \text{W}$ or Mo) was stirred at room temperature overnight. Then H_2O and Et_3OBF_4 were added. After 30 min stirring, the liquid phase was removed, the resin was washed thoroughly with H_2O , Et_2O , and THF, and then it was dried *in vacuo* at 60°C .

7a: Elemental analysis. Found: C 74.08, H 7.13, W (by ash calculated as trioxide) 10.6% (0.58 mmol/g). IR (cm^{-1}): 2040w, 1975s, 1905vs, 1860m, 1820w. ^{13}C NMR (in HMPT, with reference to $\delta(\text{HMPT}) = 36.7$): δ 322.3 ($\text{W}=\text{C}$), 207.0 and 203.6 (CO), 145.0, 128.1, 125.7, 46.0, and 40.9 (PS carrier), 65.4 and 14.3 (OEt).

7b: Ash analysis. Found: W 9.8% (0.53 mmol/g). IR (cm^{-1}): 2060w, 1974s, 1940m, 1910m, 1870m, 1820m.

7c: Ash analysis. Found: Mo 5.6% (0.58 mmol/g). IR (cm^{-1}): 2060w, 1980m, 1930s, 1865m, 1810w.

Synthesis of 9

Compound 8 was first prepared according to Fischer [6]. A dark-red solution of 0.4 g of 8 in 10 mL THF was added dropwise over 30 min to 1 g of dry 5 which was swollen in 50 mL THF. The mixture was then refluxed for ~ 17 h. After separation of the THF phase by centrifugation, the residue was washed thoroughly with THF and dried *in vacuo* to form a dark-red product. Ash analysis found W 12.4% (0.68 mmol/g). IR (cm^{-1}): 1992m, 1850vs, and 1805vs (CO), 1620s and 1598s (bipy group).

Synthesis of 11

At -78°C and in the dark, to a mixture of 4a (made from 1.4 g PS of MW 2×10^5 , containing ~ 2 mmol polyaryllithium) and 35 mL THF was added

a solution of 0.8 g of **8** in 20 mL THF. The mixture was stirred for an additional 70 min at this temperature. Then, 1.5 mL of a 1.8 *N* solution of dry HCl in Et₂O was added. After 15 min stirring at -78°C, it was warmed to room temperature. The dark-red liquid phase was removed, and the resin was washed repeatedly with cyclohexane and THF, then dried at reduced pressure. IR (cm⁻¹): 1970ms, 1935ms.

Synthesis of **15**

At -78°C a solution of *NepMgCl* in THF was rapidly added to a solution of 1/3 equivalent of PhNWCl₄·Et₂O in Et₂O. The mixture was slowly warmed to room temperature, then stirred for 24 h. The mixture was then filtered, and the magnesium salt was washed with ether. The resulting solution was concentrated to ~0.1 *M*. ¹³C NMR (in THF/Et₂O): 151.0, 149.2 (Ph, ipso), 128.3, 126.1, 125.7, 125.4 (Ph), (91.7) (CH₂), 34.7 (CMe), 31.5 (Me).

Synthesis of **16**

To a Schlenk tube which was charged with a solution of **6** (~2.5 mmol) in 10 mL THF and cooled to -40°C was added 24 mL of the above prepared 0.11 *M* solution of **15**. The solution was warmed to room temperature and stirred for 36 h. Then the mixture was centrifuged, and the solvents were removed from the supernatant. The residue was washed with dry petroleum ether, then dried, resulting in the polymeric carbene complex **16**.

Ash analysis. Found: W 20.2% (1.10 mmol/g). ¹H NMR (in THF): 89.2 (=CH-). ¹³C NMR (in THF): δ 273.0 (=CH-), 154.8, 150.5, 148.8 (Ph, ipso), (130.6), 127.6, 125.9, (122.2) (Ph), (108.1), 106.2, - (Cp), 78.3, 62.7, 41.1 (-CH₂CH(CH₂Cp)O- in the carrier), 78.5, 48.4, 44.0 (-CH₂CH(CH₂Cl)O- in the carrier), 70.4, (26.7) (-CH₂)₄O- in the carrier), 38.3, 28.5 (=CH-CMe₂-), (81.6), 37.0, 32.2 (CH₂CMe₂-).

Synthesis of **17**

A solution of **15** (0.1 *M*) was added to a THF solution of **4a** (prepared from a polystyrene resin of MW 8000) at -30 to -40°C. The mixture was warmed to room temperature slowly. After 8 h of stirring, the mixture was centrifuged and the solvents were removed from the supernatant.

Ash analysis. Found: W 17.2% (0.94 mmol/g). ¹H NMR (in THF): δ 6.8 (=CH-). ¹³C NMR (in THF): δ 272.7 (=CH-), 155.8, 151.7, 150.4, 148.5, (145.3), 145.0 (Ph, ipso), 127.6, 125.4, 124.9, 124.6 (Ph), 45.9, 40.4

($-\text{CH}_2\text{CH}-$ in the PS carrier), 38.6, 28.5 ($=\text{CH}-\text{CMe}_2$), (81.7), 36.9, 32.5 ($-\text{CH}_2\text{CMe}_2-$).

Oxidation of 7a

The complex was dispersed in THF/HMPT (3:1 v/v). The mixture was refluxed several hours until the yellow resin turned white. The liquid phase was decanted, and the resin was washed with THF, then with water, and finally dried *in vacuo*. HMPT was necessary for the reaction to proceed in the mixed solvent by improving the swelling of the resin. IR of the product (cm^{-1}): 1725 (C=O), 1190, 1160 (C-O).

Nucleophilic Substitution of the Alkoxy Group in 7a

Under nitrogen atmosphere a mixture of 7a and excess HNMe_2 (33% in H_2O) was stirred and heated to reflux for 4 h. After removing the supernatant, the resin was washed with methanol and THF and finally dried *in vacuo*. IR of the product (cm^{-1}): 1260, 800 (N-C).

Cyclopropanation of Ethyl Methacrylate

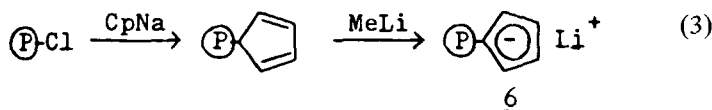
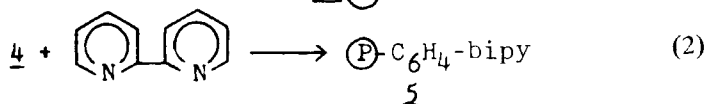
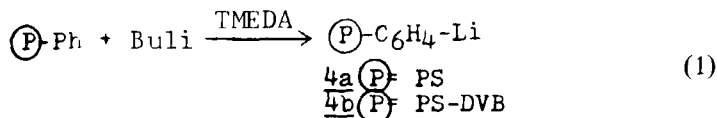
Under nitrogen, a mixture of 7a and an excess of ethyl methacrylate was stirred at reflux overnight. The resin was recovered and washed with ethanol, water, THF, and dried *in vacuo*. IR of the product (cm^{-1}): 2980 (cyclopropane ring), 1725 (C=O). 11 was similarly reacted. IR of the product (cm^{-1}): 2980, 1730.

RESULTS AND DISCUSSION

Functionalization of Polymer Carriers

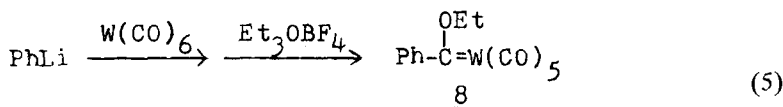
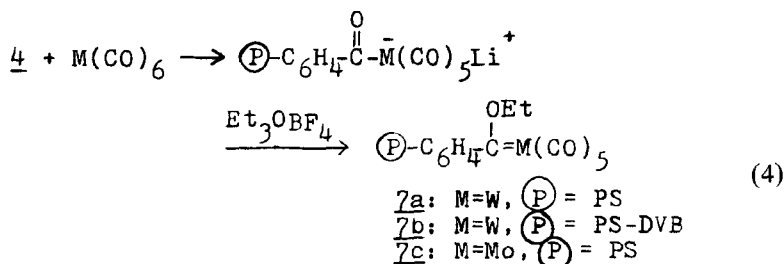
The polymeric transition-metal/carbene complexes could be formed either by attaching a metal moiety to a polymer carrier and then forming a carbene structure, or by trapping a low-molecular-weight metallocarbene with a polymer carrier. The polymers so used should have been previously functionalized. Polystyrene (PS) or its copolymer with divinylbenzene (PS-DVB) [1, 2] may serve as the carrier. These could be directly lithiated by treatment with butyllithium in the presence of tetramethylethylenediamine (TMEDA) (Eq. 1), according to Farrall [9]. Further, by treatment of the above prepared poly(styryl)lithium with 2,2-bipyridine, a bipyridine group-containing Poly-

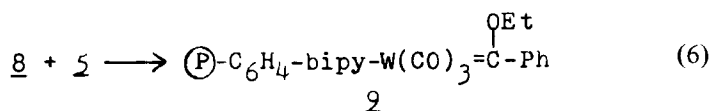
mer 5 was formed (Eq. 2) [10]. In addition, a cyclopentadienyl group-containing polymer, 6, was prepared by reacting poly(tetrahydrofuran-*co*-epi-chlorohydrin) (P(THF-*co*-ECH)) or other Cl-containing polymers with cyclopentadienyl sodium (CpNa) [11] and then with methyllithium [12] (Eq. 3).



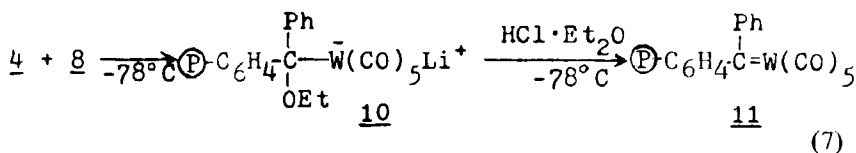
Synthesis of Polymeric Heterocarbene and Diarylcarbene Complexes

The polymeric heterocarbene complexes were synthesized by the reaction of the lithiated resin 4 with a transition metal carbonyl compound. The resulting anionic adduct was then alkylated with an oxonium salt, Et₃OBF₄ [13]. Various metallocarbenes 7a-c were obtained, depending on the type of polymer carrier and metal carbonyl (Eq. 4). Another approach to the heterocarbenes was started with phenylethoxycarbene-pentacarbonyltungsten, 8, which was prepared according to Fisher [6] from phenyllithium, W(CO)₆, and Et₃OBF₄ (Eq. 5). The substitution of two carbonyl ligands in 8 with poly(styryl)bipyridine, 5, resulted in the formation of the polymeric carbene complex 9 (Eq. 6).



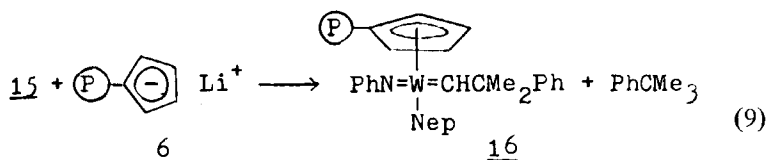
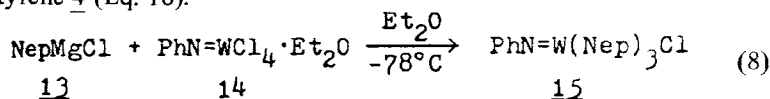


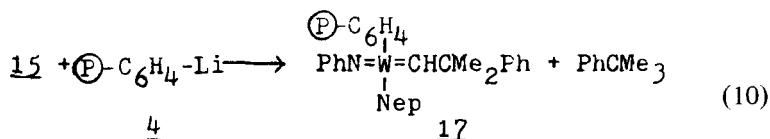
According to Casey [7], the alkoxy group in a heterocarbene complex such as 8 may undergo nucleophilic substitution with phenyllithium, giving a diarylcarbene complex. Similarly, a polymeric diarylcarbene complex, 11, was synthesized using the lithiated resin 4 as the nucleophile instead of phenyllithium (Eq. 7). During the reaction, temperatures as low as -78°C have to be maintained in order to prevent the intermediate adduct 10 from decomposition via free radicals.



Synthesis of Polymeric Alkylidene Complexes

Low molecular weight alkylidene complexes have been extensively investigated by Schrock and coworkers [8]. It was claimed that an alkyl halide possessing no β -hydrogen, such as neopentyl chloride, $\text{CMe}_3\text{CH}_2\text{Cl}$, should be used as the precursor. Instead of this expensive compound we used neophyl chloride, NepCl (12, $\text{Nep} = \text{PhCMe}_2\text{CH}_2-$), which could be easily prepared from methallyl chloride and benzene [14]. The Grignard reagent 13 prepared from NepCl was then reacted with a tungsten halide compound, 14, giving a trialkyltungsten halide complex, 15 (Eq. 8). When being attacked by a polymeric nucleophile, the Cl atom in 15 could be substituted. This would induce an α -hydrogen abstraction, forming the alkylidene structure with release of a PhCMe_3 molecule. Here, the polymeric nucleophile may be either the cyclopentadienyl-containing polymer 6 (Eq. 9) or the lithiated polystyrene 4 (Eq. 10).





Properties of the Polymeric Carbene Complexes

The polymer carriers show their influence on the physical properties of the complexes. In general, carriers of lower molecular weights offered better solubilities of the metallocarbene complexes. For example, Complexes 7a and 7c derived from a commercial polystyrene (MW 2×10^5) were soluble in hexamethylphosphoric triamide (HMPT) but only slightly soluble in THF. However, Complex 16 derived from P(THF-co-ECH) of MW 400 and Complexes 7a and 17 derived from a polystyrene of MW 8000 were very soluble in THF.

The spectroscopic studies of the complexes confirmed the carbene structures. The IR spectra of the heterocarbene complexes 7, 8, and 9 exhibited strong absorptions in the range 1800–2100 cm^{-1} due to the carbonyl ligands in the polymers. In their ^{13}C -NMR spectra the polymeric complexes displayed signals at very low magnetic field due to the carbene carbons, e.g., 7a at $\delta 322.3$, 16 at $\delta 273.0$, and 17 at $\delta 272.0$. In addition, complexes with CO ligands displayed signals at about $\delta 200$, and those with cyclopentadienyl groups at about $\delta 106$. Further, in the ^1H -NMR spectra, the alkylidene complexes 16 and 17 showed a singlet at $\delta 9.2$ and $\delta 6.8$, respectively, characteristic for the alkylidene α -protons and consistent with their low-molecular-weight analogs [8].

Differential thermogravimetry (DTG) analysis showed that the carriers stabilized the metallocarbenes to some extent, as seen in Fig. 1. The peak at 405°C on the DTG curve for Complex 7a and the peak at 418°C on that for Complex 9 were due to the polystyrene carrier. The peaks for the metallocarbene fragments in the polymeric complexes 9 and 7a were found at 220 and 170°C , respectively. These temperatures were obviously higher than that of the low-molecular-weight Complex 8 (145°C). According to Schubert [15], electron-donating groups, either at the carbene carbon or at the metal, would reduce the electron deficiency at the carbene carbon and thus stabilize the metallocarbene. This accounts for the higher stability of 9 compared to 7a.

The polymeric complexes were found to undergo chemical reactions similar to those of their low-molecular-weight analogs. The polymeric heterocarbene complexes could be oxidized in solutions by air at elevated temperatures. The oxidation product of 7a was found to be a (polystyryl)carboxylic

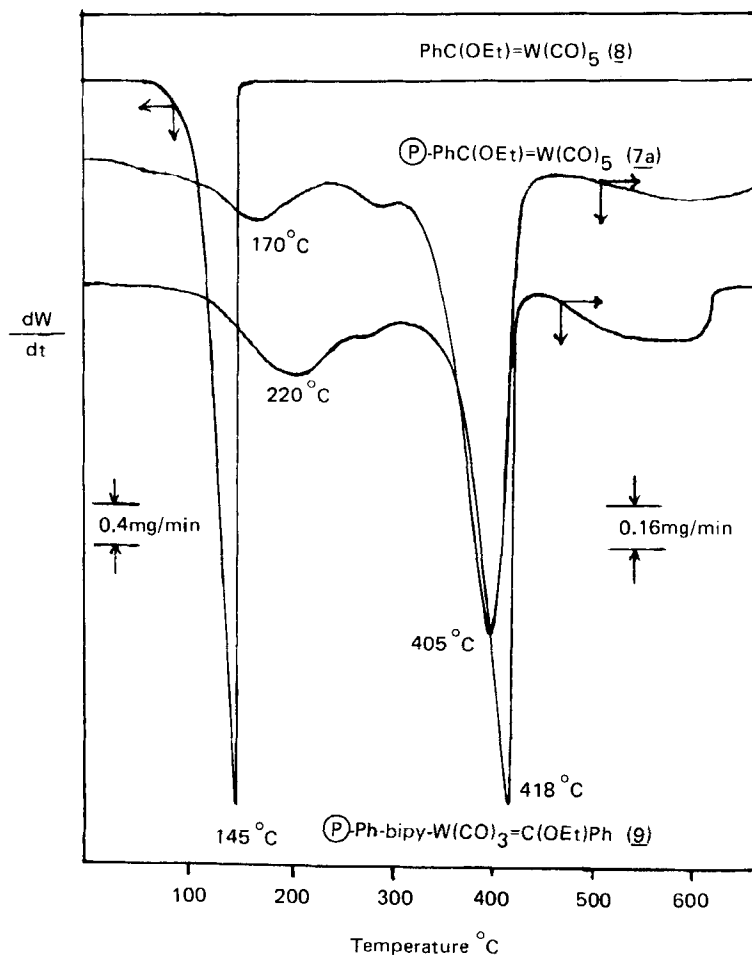
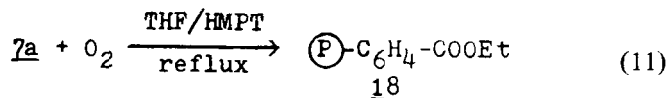
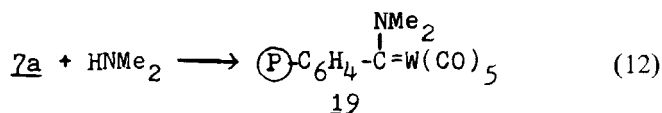


FIG. 1. DTG curves of PhC(OEt)=W(CO)₅ (8), Ⓟ-C₆H₄-C(OEt)=W(CO)₅ (7a), and Ⓟ-C₆H₄-bipy-W(CO)₃=C(OEt)Ph (9). N₂ 35 mL/min. Temperature scanning rate: 10°C/min. Sample weights: 8, 15 mg; 7a, 15 mg; 9, 14.9 mg.

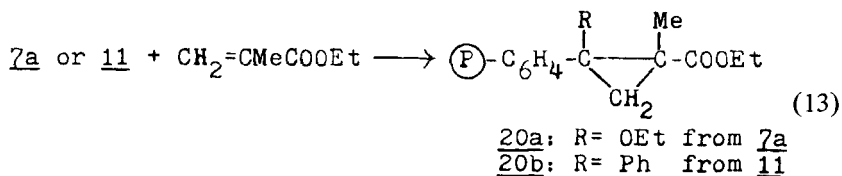
ester 18 (Eq. 11), which showed strong IR absorptions at 1725, 1190, and 1160 cm^{-1} , attributed to C=O and C–O vibrations.



When an oxo-heterocarbene complex such as 7a was attacked by a strong nucleophile, e.g., dimethylamine, the alkoxy group was substituted, forming a nitrogen heterocarbene complex 19 (Eq. 12). The structure of the product was confirmed by IR absorptions at 1260 and 800 cm^{-1} .



In addition, the polymeric complexes were found to be effective in cyclopropanation of some vinyl compounds, such as ethyl methacrylate (Eq. 13). The formation of the cyclopropane ring and carboxylate groups in 20 was indicated by IR absorptions at 2980 and 1725 cm^{-1} .



ACKNOWLEDGMENT

Support of this project by the Science Foundation of Academia Sinica and the National Natural Science Foundation of China is gratefully acknowledged.

REFERENCES

- [1] N. K. Mathur, C. K. Narang, and R. E. Williams, *Polymers as Aids in Organic Chemistry*, Academic, New York, 1980.
- [2] P. Hodge and D. C. Sherrington, *Polymer-Supported Reactions in Organic Synthesis*, Wiley, Chichester, 1980.

- [3] R. R. Schrock, in *Inorganic Chemistry: Toward the 21st Century* (ACS Symp. Ser. 211), (M. H. Chisholm, ed.), American Chemical Society, Washington, 1983, p. 363; R. R. Schrock, *Science*, **219**, 13 (1983).
- [4] K. H. Dötz, *Angew. Chem., Int. Ed. Engl.*, **23**, 587 (1984).
- [5] M. P. Doyle, *Chem. Rev.*, **86**, 919 (1986).
- [6] E. O. Fischer and A. Massböl, *Angew. Chem., Int. Ed. Engl.*, **3**, 580 (1964); E. O. Fischer and A. Massböl, *Chem. Ber.*, **100**, 2445 (1967); R. Aumann and E. O. Fischer, *Angew. Chem., Int. Ed. Engl.*, **6**, 879 (1967).
- [7] C. P. Casey, T. J. Burkhardt, C. A. Bunnell, and J. C. Calabrese, *J. Am. Chem. Soc.*, **99**, 2127 (1977).
- [8] S. F. Pedersen and R. R. Schrock, *Ibid.*, **104**, 7483 (1982).
- [9] M. J. Farrell and J. M. J. Frechet, *J. Org. Chem.*, **41**, 3877 (1976).
- [10] R. J. Card and D. C. Neckers, *Inorg. Chem.*, **17**, 2345 (1978).
- [11] H. Asai, Japanese Patent 54-15587 (1979).
- [12] W. D. Bonds Jr., C. H. Brubaker, E. S. Chandrasekaran, C. Gibbons, R. H. Grubbs, and L. C. Kroll, *J. Am. Chem. Soc.*, **97**, 2128 (1975).
- [13] H. Meerwein, *Org. Synth., Collect. Vol. V*, 1080 (1973).
- [14] W. T. Smith Jr. and J. T. Sellas, *Ibid., Collect. Vol. IV*, 702 (1963).
- [15] U. Schubert, *Coord. Chem. Rev.*, **55**, 261 (1984).
- [16] G. Wilkinson, *Org. Synth., Collect. Vol. IV*, 473 (1963).
- [17] H. Funk, W. Weiss, and G. Mohaupt, *Z. Anorg. Chem.*, **304**, 238 (1960).