ELSEVIER

Oxidative demetalation of Fischer alkoxy carbene complexes with stoichiometric pyridine *N*-oxide and NaBH₄-promoted demetalation of Fischer iminocarbene complexes with sulfur and selenium

Zhaoyan Zheng [a], Jinzhu Chen [a], Zhengkun Yu [a,*], Xiuwen Han [b]

[a] *Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 457 Zhongshan Road, Dalian, Liaoning 116023, PR China*
[b] *State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences,*
457 Zhongshan Road, Dalian, Liaoning 116023, PR China

Abstract

Oxidation of Fischer alkoxy carbene complexes were systematically investigated with stoichiometric pyridine *N*-oxide (PNO) under mild conditions, forming ester products in good to excellent yields from the corresponding monocarbene complexes. Fischer alkoxy biscarbene complexes efficiently underwent stepwise oxidative demetalation under controlled conditions, resulting in ester-monocarbene and diester products, respectively. This oxidation protocol has demonstrated a generally efficient method to oxidize Fischer alkoxy carbene complexes under mild conditions, providing a new route to novel monocarbene complexes from Fischer biscarbene complexes. In the presence of NaBH₄, reactions of Fischer iminocarbene complexes with elemental sulfur or selenium in ethanol at ambient temperature regioselectively afforded thione or selone complexes by insertion of a sulfur or selenium atom into the M=C bonds in Fischer carbene complexes, and metal-free selone was also obtained. The molecular structures of the iminocarbene complexes and selone derivatives were confirmed by X-ray crystallographic study. The NaBH₄-promoted demetalation protocol suggests a potential new route to demetalate Fischer aminocarbene complexes.
© 2006 Elsevier B.V. All rights reserved.

Keywords: Fischer carbene; Pyridine *N*-oxide; Iminocarbene; Sulfur; Selenium

1. Introduction

Over the last two decades Fischer monocarbene complexes [1] and recently biscarbene complexes [2] have been used to synthesize a wide range of organic products. Dötz benzannulation [3] and cyclopropanation [4] reactions are employed to construct functionalized phenol derivatives and cyclopropanes, respectively. Important organic synthetic methodology has also been established by Hegedus photochemical ketene generation [5]. In these reactions, the carbene carbon is directly incorporated into the skele-

ton of the newly formed products and the metal moiety is removed during the reaction. Transition metal-catalyzed transmetalations [6], carbocyclization reactions [7], and reduction of Fischer carbene complexes with metal hydrides [8] belong to this category. In other reactions such as Diels–Alder reactions [9], 1,3-dipolar cycloadditions [10] and Micheal additions [11], the transition metal-carbene carbon bond still preserves in the formed complex products, and thus a further step is necessary to remove the metal moiety.

Different procedures have been developed to remove the metal moiety and transform Fischer carbene complexes into organic products. Acid-promoted hydrolysis affords aldehydes [12]. Heating in the presence of pyridine gives enol

---

* Corresponding author. Tel./fax: +86 411 8437 9227.
  E-mail address: zkyu@dicp.ac.cn (Z.K. Yu).

ethers [9b,12b,13]. Other procedures using a variety of reagents and conditions including diazomethane [12b,14], Wittig reagents [15], chloromethyllithium [16], and hydrogenation [12b,17] have also been known to demetalate Fischer carbene complexes. In most cases, oxidation appears to be a convenient method to convert Fischer alkoxy carbene complexes into the corresponding ester products. Oxidants such as pyridine *N*-oxide (PNO) [2,18], dimethyl sulfoxide (DMSO) [12b,12c,19], dimethyldioxirane (DMD) [20], ceric ammonium nitrate (CAN) [18c,18f,19a,21], PhIO [22], and air [21c,23] have been used for this purpose. For Fischer aminocarbene complexes, harsh reaction conditions are usually required and only activated aminocarbene complexes can be oxidatively demetalated with PNO [18e]. Other reagents such as iodosobenzene (PhIO) [22], Ca(ClO)$_2$ [24], iodine [24], NaBO$_3$/KI [24], CAN [25], H$_2$O$_2$ with methyltrioxorhenium (MTO) [26], and *m*-chloroperoxybenzoic acid [27], have occasionally been reported to oxidatively demetalate Fischer aminocarbene complexes. Although oxidative demetalation is usually required in organic synthesis with Fischer carbene complexes, no systematic investigation has been well-documented in this aspect. Until recently, Barluenga et al. reported a fluoride-promoted air-oxidation method to demetalate a limited number of alkenyl and alkynyl Fischer alkoxy monocarbene complexes, resulting in ester products in low to good yields [23c]. Perdicchia et al. developed a methodology for oxidizing 1-phenyl and 1-alkyl Fischer hydrazinocarbene complexes with oxidants such as CAN, air/*hv*, Ca(ClO)$_2$, NaBO$_3$/KH$_2$PO$_4$/KI, and I$_2$ [24].

Reduction of Fischer carbene complexes has recently been paid some attention by means of reducing agents such as NaCNBH$_3$, BH$_3 \cdot$ THF, KBH(*s*Bu)$_3$, LiAlH$_4$, *i*Bu$_2$AlH, and NaBH$_4$, etc. [8]. The reported oxidants usually effect to oxidatively demetalate Fischer alkoxy carbene complexes, but only limited success has been achieved to demetalate a few activated Fischer aminocarbene complexes using the oxidation methodology [18e]. Reduction seems more versatile than oxidation to demetalate Fischer carbene complexes, affording M=C bond reduction, reduction/isomerization or reduction/(OC)$_5$M-transfer products. In some cases, functional groups in the carbene complexes can also be reduced at the same time. For reduction of Fischer aminocarbene complexes, several rare examples are presented in Scheme 1 in which the present reduction methodology demonstrates a potential route to demetalate Fischer aminocarbene complexes, but more detailed and extensive investigation is expected in this aspect. In the course of our ongoing investigation on organic synthesis *via* Fischer carbene complexes [2], removal of the metal moieties from the newly formed carbene complex products has often been required, which led us to pursue a systematic study on demetalation of different types of Fischer alkoxy carbene complexes as well as other methods to demetalate aminocarbene complexes.

Thus we chose pyridine-*N*-oxide (PNO) as the oxidant to oxidatively demetalate Fischer alkoxy carbene com-
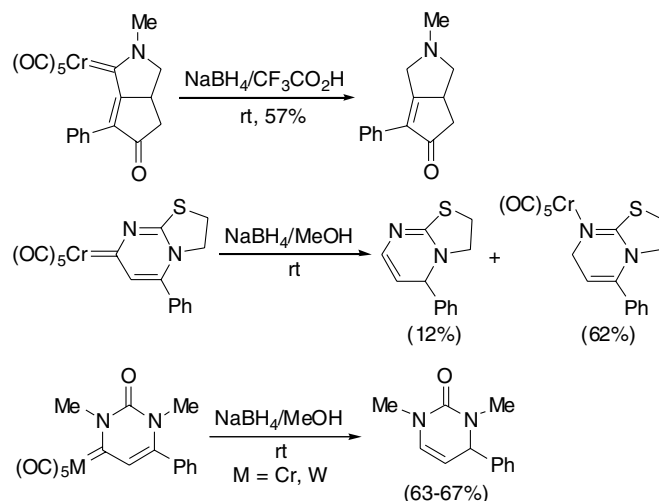
Scheme 1. Reduction of Fischer aminocarbene complexes [8b].

plexes, and used elemental sulfur and selenium to demetalate Fischer iminocarbene (which can be considered as pseudo aminocarbene) complexes in the presence of NaBH$_4$ under mild conditions. Using the oxidant system, only stoichiometric PNO is necessary for efficient removal of the (pentacarbonyl)metal moiety. With the NaBH$_4$-promoted system, sulfur or selenium insertion products and selone derivatives were selectively obtained as the products. Herein, we report a systematic study on oxidation of Fischer alkoxy monocarbene complexes and stepwise oxidation of Fischer biscarbene complexes with pyridine *N*-oxide (PNO). NaBH$_4$-promoted demetalation of Fischer iminocarbene complexes with elemental sulfur or selenium was preliminarily investigated.

2. Results and discussion

2.1. Oxidation of Fischer alkoxy carbene complexes with PNO

2.1.1. Oxidation of monocarbene complexes 1–5

The oxidation reactions of Fischer monocarbene complexes **1**–**5** were carried out with 1.0 equiv. of PNO in air at room temperature. In order to control the vigorous exothermic reactions, a solution of PNO in CH$_2$Cl$_2$ was dropwise added to the solution of a carbene complex at 0 °C,
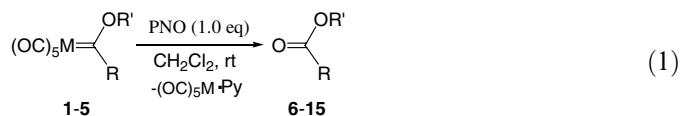
Dichloromethane was chosen as the reaction medium to avoid use of coordinative solvents such as THF and acetonitrile which can promote removal of the (pentacarbonyl)metal moiety as (OC)$_5$M · THF or (OC)$_5$M · NCCH$_3$ [1]. The oxidation reactions did not undergo without PNO in air, revealing that air itself cannot oxidize Fischer alkoxy carbene complexes under the stated conditions. Oxidation of the Fischer alkoxy carbene complexes

Table 1
Oxidation of monocarbene complexes **1–5**[a]

Entry	Carbene complex		Time (min)	Ester		Yield[b] (%)
1		**1a**	20		**6**	78
2		**1b**	20			65
3		**2a**	20		**7**	96
4		**2b**	15		**8**	77
5		**2c**	15		**9**	90
6		**3**	180		**10**	93
7		**4a**	30		**11**	93
8		**4b**	90			96
9		**4c**	60		**12**	90
10		**4d**	60			93
11		**4e**	60		**13**	70

(continued on next page)

Table 1 (*continued*)

Entry	Carbene complex		Time (min)	Ester		Yield[b] (%)
12	$(OC)_5Cr=$ OEt, CH_3	**5a**	12			81[c]
				O= OEt, CH_3	**14**	
13	$(OC)_5W=$ OEt, CH_3	**5b**	12			81[c]
14	$(OC)_5Cr=$ OEt, $CH_2CH_2CH_2CH_3$	**5c**	12			85[c]
				O= OEt, $CH_2CH_2CH_2CH_3$	**15**	
15	$(OC)_5W=$ OEt, $CH_2CH_2CH_2CH_3$	**5d**	12			82[c]

[a] Reaction conditions: carbene complex, 1.0 mmol; PNO, 1.0 mmol; CH_2Cl_2, 4 ml; room temperature (23 °C).
[b] Isolated yields (not optimized) by flash silica gel column chromatography.
[c] GC yields.

underwent very efficiently, reaching a complete conversion for the carbene complexes over a period of 0.2–3.0 h and affording ester products in good to excellent yields (up to 96%) (Table 1). It should be noted that fluoride-promoted air-oxidation of Fischer carbene complexes requires up to 36 h to achieve low to good yields (33–91%) for the ester products [23c]. The (pentacarbonyl)metal moiety was removed as $(OC)_5M \cdot py$ which was easily isolated by silica gel column chromatography [2]. 1-Alkynyl Fischer alkoxy carbene complexes **1a** and **1b** were oxidized to their corresponding ester **6** in 78% and 65% yields within 20 min (Table 1, entries 1 and 2), respectively. For 1-alkenyl carbene complexes of chromium **2a**–**c**, their corresponding ester products were obtained in 77–96% yields over a period of 15–20 min (entries 3–5), while the relatively unreactive alkenyl carbene complex **3** reached a 100% conversion within 3 h to give the organic product in 93% yield (entry 6). β-(1-Pyrazolyl)-substituted alkenyl carbene complexes **4a**–**d** were efficiently demetalated to afford esters **11** and **12** in 90–96% yields (entries 7–10), respectively. A carbene complex of chromium usually exhibited a reactivity higher than its tungsten analogue (entries 7 and 8). Somehow, ester **13** was only obtained in 70% yield from β-(1-pyrazolyl)-substituted alkenyl carbene complex **4e** (entry 11). 1-Alkyl Fischer monocarbene complexes **5a**–**d** were easily demetalated with PNO within 12 min, forming the corresponding esters in 81–85% yields (entries 12–15). It is noteworthy that the ester products from **5a**–**d** were determined by GC analysis with *n*-nonane and 1,4-dimethylbenezene as the internal standards, respectively.

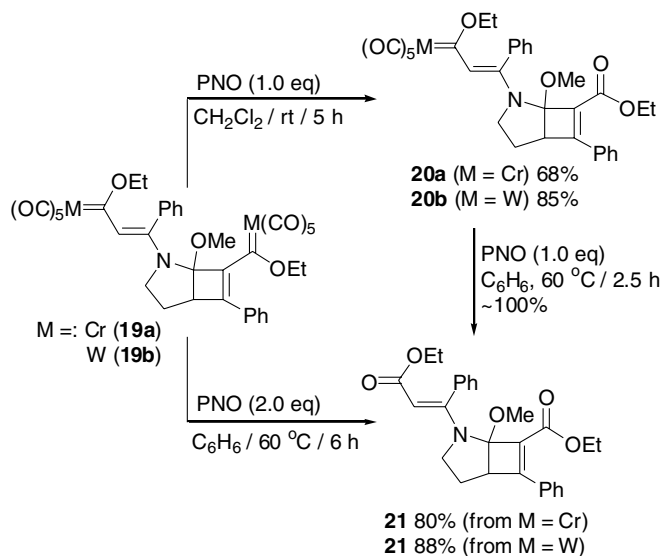### 2.1.2. Oxidation of symmetrical biscarbene complex 16

Biscarbene complex **16** was easily demetalated with PNO as the oxidant (Scheme 2). The reaction of **16** with PNO (1.0 equiv.) in air at room temperature gave a mixture of monocarbene complex **17** and diester **18** and their molar ratio varied depending on the manipulations. Lowering the
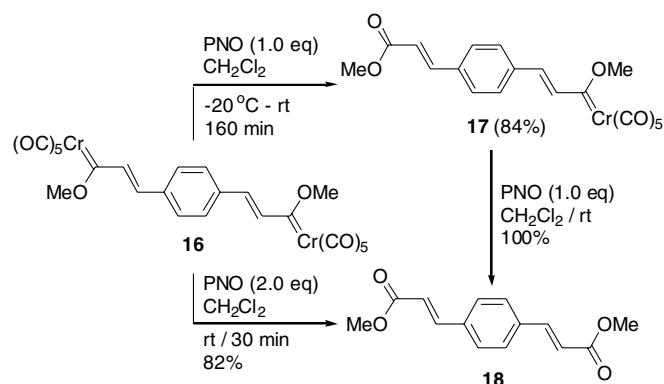
Scheme 2. Oxidation of symmetrical biscarbene complex **16**.

reaction temperature to −20 °C, the reaction of **16** and PNO in a 1:1 molar ratio predominantly afforded **17** in 84% yield with trace amount of diester **18** as the minor product. Air itself did not oxidize the biscarbene complex at low or ambient temperature. At room temperature, oxidation of **16** with 2.0 equiv. of PNO in CH_2Cl_2 afforded **18** in 82% yield, and further treatment of **17** with 1.0 equiv. of PNO quantitatively gave **18**. It should be noted that use of dilute solutions of **16** and PNO is necessary to get a good yield for the partially demetalated product, i.e., **17** (see Section 4).

### 2.1.3. Oxidation of unsymmetrical biscarbene complexes 19

Biscarbene complexes **19a** and **19b** are unstable over silica gel to get decomposed, forming monocarbene complexes with opening of the four-membered cyclobutenyl ring and removal of the $M(CO)_5$ moiety adjacent to the four-membered ring during flash column chromatography [28]. Treatment of **19** with 1.0 equiv. of PNO in CH_2Cl_2 at room temperature gave monocarbene complexes **20a** in 68% yield from **19a** (M = Cr) and **20b** in 85% yield from **19b** (M = W), respectively (Scheme 3). With 2.0 equiv. of

Scheme 3. Oxidation of unsymmetrical biscarbene complexes **19**.

PNO in benzene at an elevated temperature, i.e., 60 °C, **19** were oxidized to diester **21** in 80–88% yields. It was noticed that in all the cases, biscarbene complex of tungsten, i.e., **19b**, gave the stepwisely demetalated products, i.e., **20b** and **21**, in yields higher than its chromium analogue **19a**. Further treatment of the monocarbene complexes **20a** or **20b** in C_6H_6 at 60 °C quantitatively gave the diester **21**. Complexes **20** and diester **21** are stable over silica gel that they were conveniently isolated by flash silica gel column chromatography. It is noteworthy that in complexes **19** the M=C bond attached to the cyclobutenyl ring is more reactive to PNO than the other metal carbene bond additionally stabilized by the vinylogous nitrogen. These results imply a potential application of the present protocol in synthesis of novel Fischer mono-, bis- or polycarbene complexes by stepwise demetalation under controlled mild conditions.

2.1.4. Oxidation of aminocarbene complexes 22 and 23

Using 1-alkynyl Fischer carbene complexes **22** and **23** as the model starting complexes, oxidation of Fischer aminocarbene complexes with PNO ($\geqslant 1.0$ equiv.) were tentatively carried out under relatively harsh conditions such as extending reaction time to 10 h, at room temperature, 50 °C or 70 °C, using CH_2Cl_2, THF or CH_3CN as the reaction solvents (Scheme 4). Only in the case of **22a**, partial
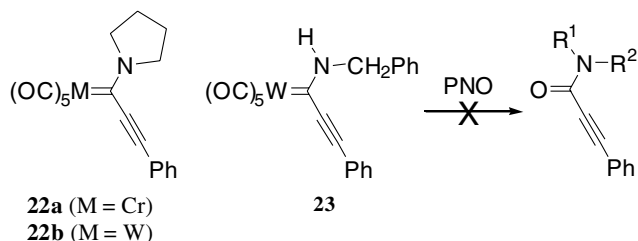
Scheme 4. Oxidation of aminocarbene complexes **22** and **23**.

oxidation occurred in CH_3CN at 70 °C over a period of 10 h, but the desired amide product failed to be isolated. In other cases, no reaction underwent and the starting carbene complexes were recovered unchanged although a couple of activated Fischer aminocarbene complexes of chromium are known to be oxidatively demetalated with PNO in THF [18e].

2.2. NaBH₄-promoted demetalation of Fischer iminocarbene complexes

With metal hydrides or borohydrides Fischer carbene complexes can be reductively demetalated, depending on the controlled conditions [8]. Complex **23** cannot react with NaCNBH₃ in methanol [8a] and complicated products are formed in the reactions of **22** and **23** with NaBH₄. A few Fischer 1-methoxy arylcarbene complexes of chromium have been known to react with elemental sulfur and selenium under relatively harsh (refluxing in ether or dioxane) conditions to form arylthiocarboxylates and arylseleno-carboxylates in 7–32% yields, respectively [29a], but so far, no further work toward demetalation of Fischer carbene complexes with a similar protocol has been pursued. Under the stated conditions [29a], Fischer aminocarbene complexes **22** or **23** did not react with elemental sulfur or selenium at ambient temperature, but we reasonably expected that elemental sulfur and selenium may be involved in the demetalation of Fischer complexes under a reduction atmosphere. Interaction of NaBH₄ with sulfur has been known to generate hydrogen sulfide [29b], reductive hydrogen sulfide or hydrogen selenide may work for demetalation of Fischer carbene complexes. In order to get regioselective demetalation products, pseudo aminocarbene complexes, i.e., Fischer iminocarbene complexes, the pyrimidine-type carbene complexes **25a** and **25b** were applied to test their demetalation with elemental sulfur and selenium in the presence of NaBH₄,
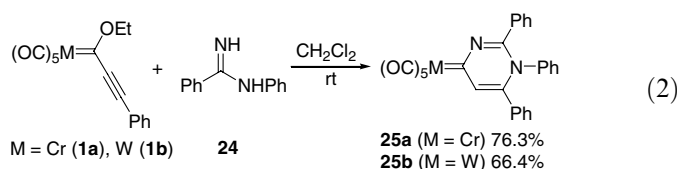
Pyrimidine-type complexes **25** were prepared in 66–76% yields by the reactions of **1** and 1.0 equiv. of N-phenyl-benzamide in CH_2Cl_2 at ambient temperature (Eq. (2)) and characterized by IR, NMR, and elemental analysis. Their molecular structures were confirmed by the X-ray single crystal structure of **25b** (Fig. 1). With NaBH₄ as the reducing agent in THF at ambient temperature, the imino group of **25** was reduced to NH–CH as shown in complexes **26**, while the metal-carbene carbon bond (M=C) stayed unchanged (Scheme 5). However, the reactions of **25** with elemental sulfur in methanol in the presence of NaBH₄ selectively generated pyrimidine-thione complexes **27** (68–89%) by the insertion of sulfur into the M=C bonds in **25**. The (pentacarbonyl)metal moiety
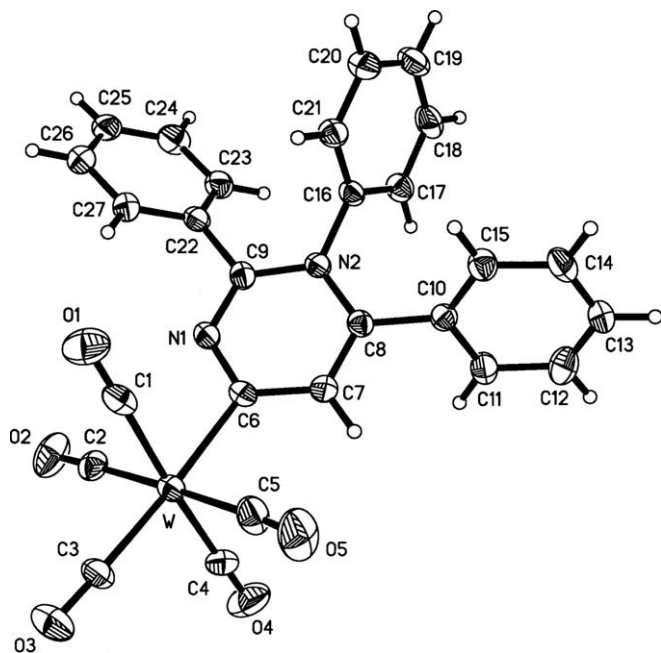
Fig. 1. Perspective view of complex **25b**.

coordinates with the sulfur atom instead of the imino nitrogen in **27**, while the same reactions in ethanol gave complicated products without elemental sulfur. Presence of sulfur during the reduction remarkably altered the selectivity of the products and stopped further reduction of the insertion products by NaBH$_4$. Isolation by flash silica gel column chromatography did not afford any other noticeable products (Scheme 5). Without S$_8$, NaBH$_4$ worked as a reducing agent to reduce the N=C bond in **25** to NH–CH as shown in **26**. Because the Fischer iminocarbene complexes are much less reactive than their alkoxy analogues, NaBH$_4$ cannot reduce the M=C bond in an iminocarbene complex to CH$_2$. Interaction of S$_8$ with NaBH$_4$ generated reductive species H$_2$S [29b] which thus

underwent insertion of S into the metal-carbene carbon bond (M=C), forming product **27**. In a fashion similar to the reactions of **25** with sulfur in the presence of NaBH$_4$, the reactions of **25** with elemental selenium in the presence of NaBH$_4$ gave the analogues of complexes **27**, i.e., pyrimidine-selone complexes **28** in 25–52% yields. At the same time, metal-free pyrimidine-selone **29** was collected (47–70%), which is attributed to the weaker coordinating ability of selenium than sulfur to chromium or tungsten (Scheme 5). Interaction of NaBH$_4$ with Se presumably formed reductive species H$_2$Se which underwent reactions with **25** in a fashion similar to H$_2$S. Thiono- and selenoesters are important reagents in organic synthesis and biochemistry [30]. The present NaBH$_4$-promoted demetalation of Fischer iminocarbene complexes provides a new route to specific thiono- and selenoamides or carboxylates.

2.3. Crystal structures of compounds 25b, 28b, and 29

The solid-state crystal structures of complexes **25b**, **28b** and pyrimidine-selone **29** were determined by X-ray crystallographic study. The crystallographic data for these compounds are summarized in Table 2, and selected bond lengths and angles in Table 3. Complex **25b** features a 1,4-dihydro-pyrimidine backbone structure with a carbene carbon atom of the W=C bond (2.207(7) Å) at the 4-position (Fig. 1). The imino nitrogen is bonded to the carbene carbon and the N=C bond length is 1.307(8) Å, while N(1)–C(6) bond length is 1.357(9) Å and much shorter than a normal C–N single bond, suggesting a delocalized C–N bond with some double bond feature. The C(7)–C(8) bond length (1.363(9) Å) is characteristic of a carbon–carbon double bond, suggesting **25b** to be an alkenyl Fischer iminocarbene complex. The structural difference between **25b** and **28b** is that a selenium atom is inserted into the W=C bond in **25b**,
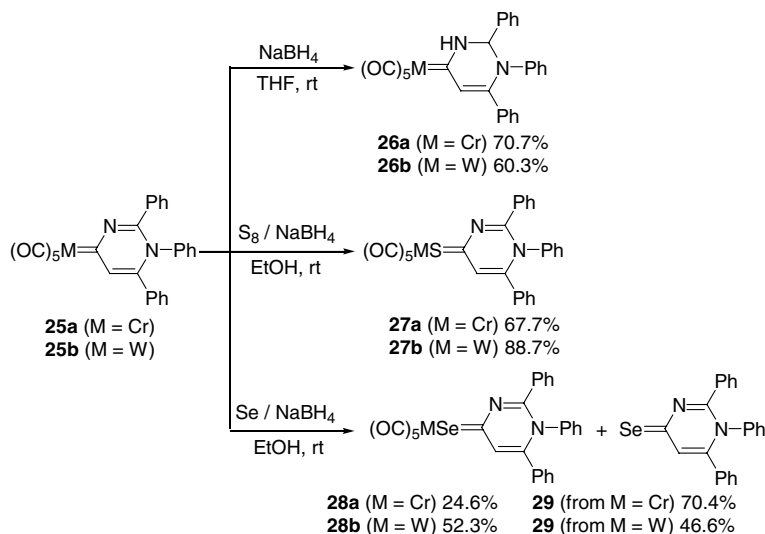
Scheme 5. NaBH$_4$-promoted demetalation of **25** with sulfur and selenium.

Table 2
Crystal data and refinement details for compounds **25b**, **28b**, and **29**

	25b	28b	29
Empirical formula	$C_{27}H_{16}N_2O_5W$	$C_{27}H_{16}N_2O_5SeW$	$C_{22}H_{16}N_2Se$
Formula weight	632.27	711.23	387.33
Temperature (K)	293(2)	293(2)	293(2)
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P2(1)/n$	Pc
a (Å)	11.0930(12)	11.1956(8)	10.5047(13)
b (Å)	11.4295(13)	22.2519(16)	9.8277(12)
c (Å)	11.8522(13)	11.3290(8)	17.937(2)
α (°)	90.492(2)	90	90
β (°)	115.403(2)	114.8450(10)	103.294(2)
γ (°)	114.633(2)	90	90
V (Å^3)	1201.3(2)	2561.1(3)	1802.1(4)
Z	2	4	4
D_c (gcm^{-3})	1.748	1.845	1.428
μ (mm^{-1})	4.848	5.971	2.089
$F(000)$	612	1360	784
Crystal size (mm^3)	$0.52 \times 0.19 \times 0.18$	$0.40 \times 0.23 \times 0.15$	$0.51 \times 0.31 \times 0.15$
θ Limits (°)	1.95–27.00	1.83–27.00	1.99–27.00
No. of data collected	7153	15085	10366
No. of unique data	5095	5532	5022
R_{int}	0.1124	0.1244	0.1321
No. of data observed with $I > 2\sigma(I)$	5095	5532	5022
No. of refined parameters	321	325	451
Goodness-of-fit on F^2	1.002	0.949	0.871
R (all data/obsd. data)	0.0536/0.0583	0.0503/0.0643	0.0588/0.0772
$_wR^2$ (all data/obsd. data)	0.1254/0.1276	0.1198/0.1252	0.1252/0.1322
Residual ρ_{max} (e Å^{-3})	2.797(−3.173)	2.447 (−1.695)	0.982 (−0.595)

Table 3
Selected bond length (Å) and angles (°) for compounds **25b**, **28b**, and **29**

Complex 25b

W–C(6)	2.207(7)	N(1)–C(6)	1.357(9)	N(1)–C(9)	1.307(8)
C(6)–C(7)	1.418(10)	C(7)–C(8)	1.363(9)	N(2)–C(8)	1.366(9)
N(2)–C(9)	1.375(8)	N(2)–C(16)	1.465(8)		
N(1)–C(6)–W	118.4(5)	C(7)–C(6)–W	126.0(5)	C(6)–N(1)–C(9)	121.6(6)
N(1)–C(6)–C(7)	115.5(6)	N(1)–C(9)–N(2)	122.8(6)	C(9)–N(2)–C(8)	118.3(5)
N(2)–C(8)–C(7)	118.4(6)	C(6)–C(7)–C(8)	121.7(7)		

Complex 28b

W–Se	2.6568(8)	Se–C(6)	1.835(6)	N(2)–C(9)	1.299(8)
N(2)–C(6)	1.352(8)	N(1)–C(9)	1.364(8)	N(1)–C(8)	1.388(8)
N(1)–C(22)	1.453(8)	C(6)–C(7)	1.421(9)	C(7)–C(8)	1.340(9)
C(6)–Se–W	110.6(2)	N(2)–C(6)–Se	121.0(5)	N(2)–C(6)–C(7)	119.2(6)
C(6)–N(2)–C(9)	119.4(6)	N(2)–C(9)–N(1)	123.8(6)	C(9)–N(1)–C(8)	118.2(5)
C(7)–C(8)–N(1)	119.0(6)	C(6)–C(7)–C(8)	119.9(6)		

Compound 29

Se(1)–C(6)	1.843(6)	N(1)–C(9)	1.334(9)	N(1)–C(6)	1.387(9)
N(2)–C(9)	1.352(9)	N(2)–C(8)	1.388(9)	C(6)–C(7)	1.383(10)
C(7)–C(8)	1.363(9)				
N(1)–C(6)–Se(1)	118.0(5)	C(6)–N(1)–C(9)	117.7(6)	N(1)–C(9)–N(2)	123.8(7)
C(9)–N(2)–C(8)	119.1(6)	N(2)–C(8)–C(7)	118.2(6)	C(8)–C(7)–C(6)	121.0(7)
N(1)–C(6)–C(7)	119.4(6)				

thus generating **28b** (Fig. 2). In complex **28b**, the W–Se, C–Se and C(7)–C(8) bond lengths are 2.6568(8) Å, 1.835(6) Å, and 1.340(9) Å, demonstrating a coordinative bond, a C=Se bond, and a carbon–carbon double bond, respectively. The imino N(2)–C(9) bond (1.299(8) Å) almost stays unchanged in **28b** as compared with that in its analogue **25b**. The C(6)–Se–W angle is 110.6(2)°

with the W(CO)$_5$ moiety bending to the imino nitrogen, which may effect long-range interaction with the metal atom. In pyrimidine-selone **29** (Fig. 3), All the C(6)–Se(1) (1.843(6) Å), imino N(1)–C(9) (1.334(9) Å), and C(7)–C(8) (1.363(9) Å) bond lengths are a little bit longer than their corresponding analogues in **28b**, implying that the molecular structure of **28b** is repelled by the W(CO)$_5$
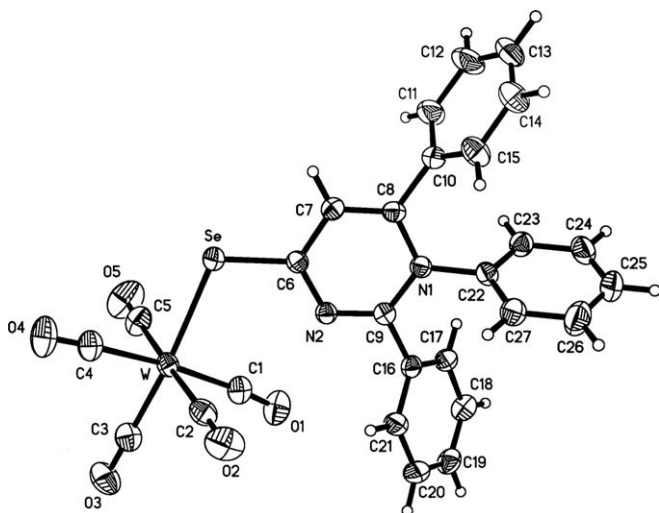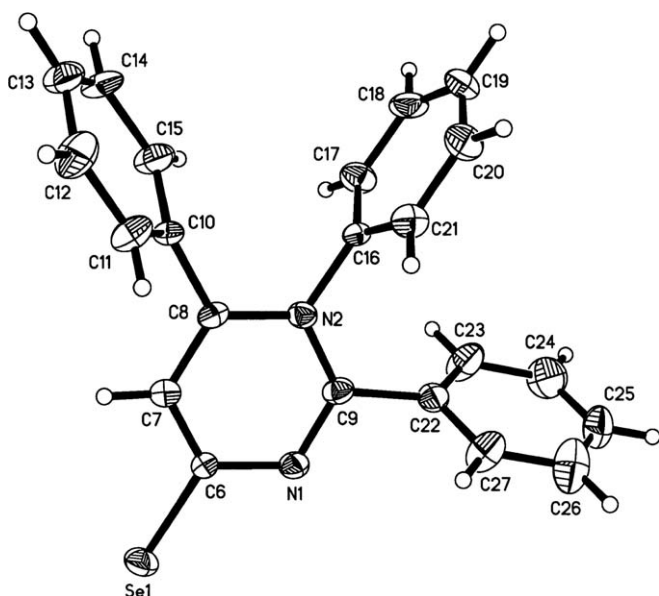
Fig. 2. Perspective view of complex **28b**.

Fig. 3. Perspective view of pyrimidine-selone **29**.

moiety coordinating to the selenium atom, shortening the related bonds in **28b**.

3. Summary

In summary, the oxidation protocol for demetalation of Fischer alkoxy carbene complexes with stiochiometric pyridine *N*-oxide (PNO) can be applied to both mono- and biscarbene complexes under mild conditions. Stepwise oxidation of Fischer alkoxy biscarbene complexes was realized with PNO under controlled conditions, providing a new route to novel Fischer alkoxy monocarbene complexes. In the presence of NaBH$_4$, reactions of Fischer iminocarbene complexes with elemental sulfur or selenium regioselectively afforded thiones or selones. This NaBH$_4$-promoted protocol suggests a potential new route to demetalate Fischer aminocarbene complexes.

4. Experimental

4.1. General considerations

All the oxidation reactions were carried out in air unless otherwise stated and the NaBH$_4$-involved reactions were pursued under a nitrogen atmosphere. Reaction solvents were dried and distilled prior to use by the literature methods. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a Bruker DRX-400 spectrometer and all chemical shift values refer to $\delta_{TMS} = 0.00$ ppm or CDCl$_3$ (δ(^{1}H), 7.26 ppm; δ(^{13}C), 77.16 ppm). IR spectra were recorded on a Bruker Tensor 27 FT-IR spectrophotometer. Elemental analysis was achieved by the Analysis Center, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences. Analytical TLC plates, Sigma-Aldrich silica gel 60$_{F200}$ were viewed by UV light (254 nm). Chromatographic purifications were performed on SDZF silica gel 160. Fischer carbene complexes **1** [31], **2** [32], **3** [32], **4** [1e,11b], **5** [33], **16** [32] and **19** [28] were prepared as reported. NMR spectroscopic data for the oxidation products **6** [34], **7** [35], **8** [36], **9** [37], **10** [38] and **18** [39] were previously reported.

4.2. A typical procedure for oxidation of Fischer alkoxy carbene complexes

A pre-cooled-to-0 °C solution of pyridine *N*-oxide (95 mg, 1.0 mmol) in 2 ml of CH$_2$Cl$_2$ was added to the solution of carbene complex **2a** (338 mg, 1.0 mmol) in 2 ml of CH$_2$Cl$_2$ in a 5-ml screwtop vessel at 0 °C over a period of 2 min. After the addition was complete, the reaction mixture was warmed up to room temperature and stirred until all the carbene complex was consumed by TLC analysis. The resultant mixture was diluted with CH$_2$Cl$_2$, filtered through a short pad of celite, and then concentrated under reduced pressure. Purification by flash silica gel column chromatography with the eluent petroleum ether (30–60 °C)/CH$_2$Cl$_2$ (v/v, 6/1) afforded the ester product **7** as white solid (156 mg, 96%). The known products were characterized by ^{1}H and ^{13}C{^{1}H} NMR and comparison with the reported NMR data or by comparison of their GC traces with those of the authentic samples. The new products were fully characterized by ^{1}H and ^{13}C{^{1}H} NMR, IR, and elemental analysis. Stepwise oxidation of Fischer biscarbene complexes was carried out under controlled conditions as described in the Supporting Information.

### 4.3. Stepwise oxidation of symmetrical biscarbene complex 16

(a) *Partial oxidation*: A solution of pyridine *N*-oxide (24 mg, 0.25 mmol) in 20 ml of CH$_2$Cl$_2$ was added dropwise to the solution of biscarbene complex **16** (150 mg, 0.25 mmol) in 20 ml of CH$_2$Cl$_2$ at −20 °C over a period of 40 min. The reaction mixture was allowed to warm to room temperature and stirred for 2 h to get a complete conversion of **16** by TLC analysis. All the volatiles were

removed under reduced pressure. Purification by flash silica gel column chromatography (petroleum ether/CH_2Cl_2, v/v = 3:1) afforded complex **17** as red crystals (89 mg, 84%). M.p.: 74–75 °C. (b) *Complete oxidation*: A solution of pyridine *N*-oxide (72 mg, 0.76 mmol) in 2 ml of CH_2Cl_2 was added to the solution of biscarbene complex **16** (228 mg, 0.38 mmol) in 2 ml CH_2Cl_2 at room temperature. The reaction was finished within 30 min by TLC analysis, and all the volatiles were removed under reduced pressure. Purification by flash silica gel column chromatography (petroleum ether/CH_2Cl_2, v/v = 1:1) afforded diester **18** as white solid (77 mg, 82%).

4.4. Stepwise oxidation of unsymmetrical biscarbene complex 19a

(a) *Partial oxidation*: A solution of pyridine *N*-oxide (24 mg, 0.25 mmol) in 2 ml of CH_2Cl_2 was added to the solution of **19a** (200 mg, 0.25 mmol) in 2 ml of CH_2Cl_2 in a 5-ml screwtop vessel at room temperature. The reaction was finished over a period of 5 hours by TLC analysis. Purification by flash silica gel column chromatography (petroleum ether/CH_2Cl_2, v/v = 2:1) afforded complex **20a** as red crystals (106 mg, 68%). (b) *Complete oxidation*: A mixture of pyridine *N*-oxide (95 mg, 1.0 mmol) and complex **19a** (400 mg, 0.5 mmol) in 20 ml benzene was stirred at 60 °C for 6 hours. Work-up as mentioned above gave diester **21** as colorless crystals (180 mg, 80%).

4.5. 3-(3′,4′,5′-Trimethylpyrazol-1′-yl)- 3-phenyl-acrylic acid ethyl ester (11)
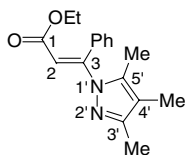
(a) 2-Ethoxy-4-phenyl-4-(3′,4′,5′-trimethylpyrazol-1′-yl)-1,1,1,1,1-pentacarbonyl-1-chroma-1,3-butadiene **4a** (460 mg, 1.0 mmol) was reacted with PNO (95 mg, 1.0 mmol) to afford **11** as white solid (264 mg, 93%). (b) 2-Ethoxy-4-phenyl-4-(3′,4′,5′-trimethylpyrazol-1′-yl)-1,1,1,1,1-pentacarbonyl-1-tungsta-1,3-butadiene **4b** (592 mg, 1.0 mmol) was reacted with PNO (95 mg, 1.0 mmol) to afford **11** as white solid (273 mg, 96%). M.p.: 54 °C. ^{1}H NMR (CDCl$_3$, 23 °C, 400 MHz): δ 7.42–7.33 (m, 5H, 3-Ph), 6.27 (s, 1H, 2-H), 4.07 (q, 2H, OCH$_2$), 2.22 (s, 3H, 5′-CH$_3$), 1.88 (s, 3H, 3′-CH$_3$), 1.64 (s, 3H, 4′-CH$_3$), 1.13 (t, 3H, OCH$_2$CH$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$, 23 °C): δ 165.63 (Cq, C1), 151.14 (Cq, C5′), 149.58 (Cq, C3′), 137.79 (Cq, C3), 134.4 (Cq, *i*-C of 3-Ph), 129.80, 129.58 and 127.88 (1:2:2 CH, 3-Ph), 115.58 (Cq, C4′), 111.66 (CH, C2), 59.85 (OCH$_2$), 13.89 (OCH$_2$CH$_3$), 11.92 (3′-CH$_3$), 11.21 (5′-CH$_3$), 7.96 (4′-CH$_3$). IR (KBr) cm^{-1}: 1712.7 (60) [v (C=O)], 1624.0 (60),

1589.3 (50), 1496.7 (40), 1446.5 (40) [v (C=C, C=N)]. Anal. Calc. for: C$_{17}$H$_{20}$N$_2$O$_2$: C, 71.81; H, 7.09; N, 9.85. Found: C, 71.94; H, 6.90; N, 9.83%.

4.6. 3-(4′-Benzyl-3′,5′-dimethylpyrazol-1′-yl)-3-phenyl-acrylic acid ethyl ester (12)
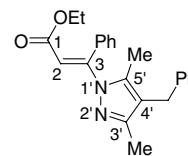
(a) 2-Ethoxy-4-phenyl-4-(3′,5′-dimethyl-4′-benzylpyrazol-1′-yl)-1,1,1,1,1-penta carbonyl-1-chroma-1,3-butadiene **4c** (536 mg, 1.0 mmol) was reacted with PNO (95 mg, 1.0 mmol) to afford **12** as white solid (328 mg, 90%). (b) 2-Ethoxy-4-phenyl-4-(3′,5′-dimethyl-4-benzylpyrazol-1′-yl)-1,1,1,1,1-pentacarbonyl-1-tungsta-1,3-butadiene **4d** (668 mg, 1.0 mmol) was reacted with PNO (95 mg, 1.0 mmol) to afford **12** as white solid (336 mg, 93%). M.p.: 62 °C. ^{1}H NMR (CDCl$_3$, 23 °C, 400 MHz): δ 7.44–7.37, 7.28, 7.19 and 7.09 (m each, 5:2:1:2H, 2 × Ph), 6.35 (s, 1H, 2-H), 4.09 (q, 2H, OCH$_2$), 3.71 (s, 2H, 4′-CH$_2$), 2.17 (s, 3H, 5′-CH$_3$), 1.68 (s, 3H, 3′-CH$_3$), 1.15 (t, 3H, OCH$_2$CH$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$, 23 °C): δ 165.74 (C$_q$, C1), 151.12 (Cq, C5′), 149.94 (Cq, C3′), 140.05 (Cq, C3), 138.86 and 134.45 (C$_q$ each, *i*-C of 2 × Ph), 130.06, 19.71, 18.49, 128.13, 128.00, and 126.08 (CH of 2 × Ph), 118.87 (C$_q$, C4′), 112.61 (C2), 60.14 (OCH$_2$), 29.29 (CH$_2$Ph), 14.08 (OCH$_2$CH$_3$), 12.31 and 11.52 (5′- and 3′-CH$_3$). IR (KBr) cm^{-1}: 1714.6 (65) [v (C=O)], 1626.0 (60), 1585.4 (40), 1494.7 (30), 1444.6 (30) [v (C=C, C=N)]. Anal. Calc. for: C$_{23}$H$_{24}$N$_2$O$_2$: C, 76.64; H, 6.71; N, 7.77. Found: C, 76.90; H, 6.87; N, 7.64%.

4.7. 3-(3′,5′-Dimethylpyrazol-1′-yl)-3-phenyl-acrylic acid ethyl ester (13)
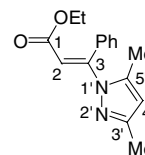
2-Ethoxy-4-phenyl-4-(3′,5′-dimethylpyrazol-1′-yl)-1,1,1,1,1-pentacarbonyl-1-tungsta-1,3-butadiene **4e** (578 mg, 1.0 mmol) was reacted with PNO (95 mg, 1.0 mmol) to afford **13** as pale yellow solid (190 mg, 70%). M.p.: 67 °C. ^{1}H NMR (CDCl$_3$, 23 °C, 400 MHz): δ 7.44–7.33 (m, 5H, Ph), 6.32 (s, 1H, 2-H), 5.92 (s, 1H, 4′-H), 4.07 (q, 2 H, OCH$_2$), 2.26 and 1.71 (s each, 3:3H, 5′- and 3′-CH$_3$), 1.14 (t, 3H, OCH$_2$CH$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$, 23 °C): δ 165.78 (C$_q$, C1), 151.03 (Cq, C5′), 150.32 (Cq, C3′), 141.91 (Cq, C3), 134.3 (Cq, *i*-C of Ph), 130.15, 129.76 and 128.19 (1:2:2 CH, Ph), 112.90 (C4′), 109.57 (C2), 60.25 (OCH$_2$), 14.12 (OCH$_2$CH$_3$), 13.69 and 12.99

(3′- and 5′-CH$_3$). IR (KBr) cm^{-1}: 1728.1 (80) [v (C=O)], 1633.6 (85), 1562.3 (80), 1496.7 (55), 1448.5 (50) [v (C=C, C=N)]. Anal. Calc. for: C$_{16}$H$_{18}$N$_2$O$_2$: C, 71.09; H, 6.71; N, 10.36. Found: C, 71.05; H, 6.81; N, 10.30%.

4.8. 2-Methoxy-4-(3′-phenyl acrylic acid methyl ester)-1,1,1,1,1-pentacarbonyl-1- chroma-1,3-butadiene (17)
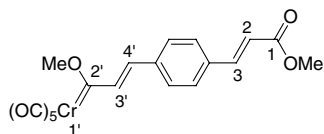
Red crystals. M.p.: 74–75 °C. ^{1}H (CDCl$_3$, 23 °C, 400 MHz): δ 7.58 (m, 4H, aromatic CH), 7.98 and 6.91 (AB, 2H, $J = 11.3$ Hz), 7.69 and 6.50 (AB, 2H, $J = 11.9$ Hz), 4.84 (s, 3H, 2′-OCH$_3$), 3.83 (s, 3H, 1-OCH$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$, 23 °C): δ 333.66 (Cq, Cr=C, C2′), 224.42 and 216.70 (Cq, 1:4, *trans*- and *cis*-CO, Cr(CO)$_5$), 167.28 (Cq, C1), 143.73 (CH, C3), 140.06 (CH, C4′), 136.65 and 136.51 (Cq, *i*-C of C$_6$H$_4$), 129.94 and 128.81 (CH of C$_6$H$_4$), 127.82 (CH, C3′), 119.28 (CH, C2), 66.67 (1-OCH$_3$), 51.99 (2′-OCH$_3$). IR (KBr) cm^{-1}: 2056.0 (100) and 1915.2 (100) [v (C≡O)], 1712.7 (95) [v(C=O)]. Anal. Calc. for C$_{19}$H$_{14}$CrO$_8$: C, 54.04; H, 3.34. Found: C, 53.38; H, 3.59%.

4.9. 2-(1,1,1,1,1-Pentacarbonyl-2-ethoxy-4-phenyl-1-chroma-4-buta-1,3-dienyl)-1-methoxy-6-phenyl-2-azabicyclo-[3.2.0]hept-6-ene-7-carboxylic acid ethyl ester (20a)
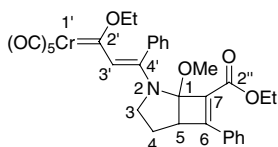
Red crystal (106 mg , 68%), M.p. >118 °C, dec. ^{1}H NMR (CDCl$_3$, 23 °C, 400 MHz): δ 7.95 (s, 1H, 3′-H), 7.97–7.93 and 7.34 (m each, 2:3H, 6-Ph), 7.44 and 7.09 (m each, 3:2H, 4′-Ph), 4.41 and 4.21 (q each, 1:1 H, 2′-OCH$_2$), 4.31 (m, 2H, 2″-OCH$_2$), 3.77 (d, 1H, $J = 5.7$ Hz, 5-H), 3.62 (s, 3H, 1-OCH$_3$), 3.17 and 3.08 (m each, 1:1H, 3-H$_2$), 1.85 and 1.76 (m each, 1:1 H, 4-H$_2$), 1.34 (t, 3H, 2″-OCH$_2$CH$_3$), 0.62 (t, 3H, 2′-OCH$_2$CH$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$, 23 °C): δ 306.26 (Cq, Cr=C, C2′), 224.76 and 218.71 (Cq each, 1:4, *trans*- and *cis*-CO, Cr(CO)$_5$), 162.11 (Cq, C2″), 154.20 (Cq, C6), 149.20 (Cq, C4′), 139.61 (Cq, *i*-C of 4′-Ph), 130.66 (Cq, *i*-C of 6-Ph), 131.46, 129.66, 128.83, 128.54, 128.04, 127.76 (CH of 2 × Ph), 127.20 (Cq, C7), 123.27 (CH, C3′), 96.9 (Cq, C1), 73.88 (2′-OCH$_2$), 61.20 (2″-OCH$_2$), 53.00 (1-OCH$_3$), 49.88 (CH, C5), 49.66 (CH$_2$, C3), 23.25 (CH$_2$, C4), 14.40 (2″-OCH$_2$CH$_3$), 14.17 (2′-OCH$_2$CH$_3$). IR (KBr), cm^{-1}:

2048.3 (15), 1913.3 (50) [v (C≡O)], 1689.5 (10) [v(C=O)], 1489.0 (20) [v (C=C)]. Anal. Calc. for C$_{32}$H$_{29}$CrNO$_9$: C, 61.64; H, 4.69; N, 2.25. Found: C, 61.39; H, 4.74; N, 2.06%.

4.10. 2-(1,1,1,1,1-Pentacarbonyl-2-ethoxy-4-phenyl-1-tungsta-4-buta-1,3-dienyl)-1-methoxy-6-phenyl-2-azabicyclo-[3.2.0]hept-6-ene-7-carboxylic acid ethyl ester (20b)
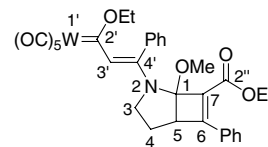
Orange crystals (161 mg, 85%), M.p. >123 °C, dec. ^{1}H NMR (CDCl$_3$, 23 °C, 400 MHz): δ 8.02 (s, 1H, 3′-H), 7.94 and 7.35 (m each, 2:3H, 6-Ph), 7.44 and 7.11 (m each, 3:2H, 4′-Ph), 4.43 and 4.32 (q each, 1:1 H, 2″-OCH$_2$), 4.13 (m, 2H, 2′-OCH$_2$), 3.78 (d, 1H, $J = 5.7$ Hz, 5-H), 3.62 (s, 3H, 1-OCH$_3$), 3.20 and 3.07 (m each, 1:1H, 3-H$_2$), 1.86 and 1.79 (m each, 1:1H, 4-H$_2$), 1.35 (t, 3H, 2″-OCH$_2$CH$_3$), 0.61 (t, 3H, 2′-OCH$_2$CH$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$, 23 °C): δ 281.68 (Cq, W=C, C2′), 204.63 and 199.48 (Cq, 1:4, *trans*- and *cis*-CO, W(CO)$_5$), 161.91 (Cq, C2″), 154.31 (Cq, C6), 152.87 (Cq, C4′), 139.65 (Cq, *i*-C of 4′-Ph), 130.50 (Cq, *i*-C of 6-Ph), 131.49, 129.62, 128.79, 128.44, 128.08, and 127.11 (CH of 2 × Ph), 127.41 (Cq, C7), 125.46 (CH, C3′), 96.87 (Cq, C1), 76.40 (2′-OCH$_2$), 61.15 (2″-OCH$_2$), 53.01 (1-OCH$_3$), 49.88 (CH, C5), 49.58 (CH$_2$, C3), 23.11 (CH$_2$, C4), 14.42 (2″-OCH$_2$CH$_3$), 13.99 (2′-OCH$_2$CH$_3$). IR (KBr) cm^{-1}: 2057.9 (90), 1905.6 (100) [v (C≡O)], 1691.5 (70) [v (C=O)], 1485.1 (90) [v (C=C)]. Anal. Calc. for: C$_{32}$H$_{29}$NO$_9$W: C, 50.88; H, 3.87; N, 1.85. Found: C, 50.76; H, 3.79; N, 1.80%.

4.11. 1-Methoxy-6-phenyl-2-azabicyclo-[3.2.0]hept-6-ene-2,7-dicarboxylic acid ethyl ester (21)
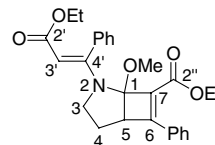
Colorless crystals. M.p.: 123 °C. ^{1}H (CDCl$_3$, 23 °C, 400 MHz): 7.96 and 7.38 (m each, 2:3H, 6-Ph), 7.43 and 7.21 (m each, 3:2H, 4′-Ph), 6.22 (s, 1H, 3′-H), 4.36 (q, 2H, 2″-OCH$_2$), 3.93 (m, 2H, 2′-OCH$_2$), 3.71 (d, 1H, $J = 5.7$ Hz, 5-H), 3.55 (s, 3H, 1-OCH$_3$), 3.17 and 2.94 (m each, 1:1H, 3-H$_2$), 1.78 and 1.71 (m each, 1:1H, 4-H$_2$), 1.44 (t, 3H, 2″-OCH$_2$CH$_3$), 1.10 (t, 3H, 2′-OCH$_2$CH$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$, 23 °C): δ 168.04 (Cq, C2′), 163.20 (Cq, C2″), 158.19 (Cq, C4′), 154.58 (Cq, C6), 138.25 (Cq, *i*-C of 4′-Ph), 130.99 (Cq, *i*-C of 6-Ph), 131.13, 129.58, 128.76, 128.32, 128.08, and 127.58 (CH of 2 × Ph), 127.89 (Cq, C7), 95.62 (Cq, C1), 94.01 (CH,

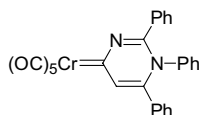C3′), 61.31 (2″-OCH₂), 58.63 (2′-OCH₂), 52.45 (1-OCH₃), 50.20 (CH, C5), 49.40 (CH₂, C3), 23.12 (CH₂, C4), 14.45 (2″-OCH₂CH₃), 14.14 (2′-OCH₂CH₃). IR (KBr) cm⁻¹: 1693.4 (30), 1581.5 (35) [ν(C=O)], 1492.8 (10) [ν (C=C)]. Anal. Calc. for C₂₇H₂₉NO₅: C, 72.46; H, 6.53; N, 3.13. Found: C, 72.42; H, 6.51; N, 3.03%.

*4.12. Synthesis of 4-(1,1,1,1,1-pentacarbonyl-1-chroma)-1,2,6-triphenyl-1,4-dihy dropyrimidine (**25a**)*

1-Alkynyl carbene complex **1a** (0.5 mmol) was reacted with *N*-phenyl-benzamidine **24** (0.5 mmol) in 3 mL of dry dichloromethane in a 5-mL screwtop vessel with stirring at ambient temperature and the reaction was monitored by TLC on silica gel. After **1a** was completely consumed, all the volatiles were removed under reduced pressure. The resultant residue was purified by flash silica gel chromatography (v/v, hexanes/CH₂Cl₂ = 1:1) afforded **25a** as red crystals (191 mg, 76.3%). Single crystals were obtained by recrystallization from CH₂Cl₂/pentane at −20 °C. M.p.: 160 °C (dec.); ¹H NMR (CDCl₃, 23 °C, 400 MHz) δ 8.36 (s, 1H, 5-H), 7.41, 7.32, 7.29–7.16, 7.10 and 6.93 (m each, 2:2:7:2:2H, 3 × Ph); ¹³C{¹H} NMR (CDCl₃, 23 °C) δ 281.05 (s, Cq, Cr=C), 227.09 and 219.57 (Cq each, 1:4, *trans*- and *cis*-CO, Cr(CO)₅), 144.05 and 138.87 (Cq each, C2 and C6), 138.23, 134.18 and 132.04 (Cq each, *i*-C of 3 × Ph), 137.39 (C5), 130.58, 130.25, 129.92, 129.50, 129.39, 128.69, 128.61, and 128.13 (CH of 3 × Ph); IR (KBr) cm⁻¹: 2046 (35), 1921 (55), 1889 (50) [ν (C≡O)], 1543 (25) [ν (C=N)], 1585 (20), 1443 (20) [ν (C=C)]. Anal. Calc. for C₂₇H₁₆CrN₂O₅: C, 64.80; H, 3.22; N, 5.60. Found: C, 64.63; H, 3.33; N, 5.37%.

*4.13. Synthesis of 4-(1,1,1,1,1-pentacarbonyl-1-tungsta)-1,2,6-triphenyl-1,4-dihydropyrimidine (**25b**)*
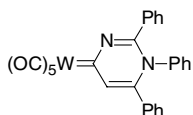
In a fashion similar to synthesis of **25a**, the reaction of **1b** (0.5 mmol) with **24** (0.5 mmol) gave **25b** as red crystals (210 mg, 66.4 %). Single crystals suitable for X-ray crystallographic study were obtained by recrystallization from CH₂Cl₂/pentane at −20 °C. M.p.: 166–168 °C; ¹H NMR (CDCl₃, 23 °C, 400 MHz) δ 8.32 (s, 1H, 5-H), 7.40, 7.35, 7.29–7.23, 7.18, 7.11 and 6.94 (m each, 2:2:5:2:2:2H, 3 × Ph); ¹³C{¹H} NMR (CDCl₃, 23 °C) δ 256.03 (Cq, W=C), 207.36 and 200.73 (Cq each, 1:4, *trans*- and *cis*-CO, W(CO)₅), 147.66 and 142.20 (Cq each, C2 and C6),

139.43 (C5), 138.41, 134.15 and 132.08 (Cq each, *i*-C of 3 × Ph), 130.46, 130.29, 129.96, 129.62, 129.41, 129.24, 128.63, 128.54 and 128.16 (2:1:1:1:2:2:2:2:2 CH, 3 × Ph); IR (KBr) cm⁻¹: 2054 (70), 1917 (85), 1878 (85) [ν (C≡O)], 1543 (60) [ν (C=N)], 1473 (50) [ν (C=C)]. Anal. Calc. for C₂₇H₁₆N₂O₅W: C, 51.29; H, 2.55; N, 4.43. Found: C, 51.18; H, 2.71; N, 4.20%.

*4.14. Synthesis of 4-(1,1,1,1,1-pentacarbonyl-1-chroma)-1,2,6-triphenyl-1,2,3,4-tetrahydropyrimidine (**26a**)*
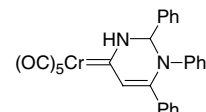
Complex **25a** (250 mg, 0.5 mmol) and sodium borohydride (19 mg, 0.5 mmol) were added to a solution of THF (10 mL), and the mixture was vigorously stirred at ambient temperature under nitrogen atmosphere. The reaction was monitored by TLC on silica gel. After **25a** was completely consumed over a period of 5 h, all the volatiles were removed under reduced pressure. The resultant residue was purified by flash silica gel column chromatography (v/v, hexanes/CH₂Cl₂ = 1:1) afforded **26a** as orange crystals (178 mg, 70.7%). Single crystals were obtained by recrystallization from CH₂Cl₂/pentane at −20 °C. M.p.: 144–145 °C; ¹H NMR (CDCl₃, 23 °C, 400 MHz) δ 8.30 (br, 1H, 5-H), 7.69, 7.59, 7.53–7.40, 7.37–7.26, 7.16, and 7.06 (m each, 2:2:3:5:1:2H, 3 × Ph), 7.01 and 6.24 (s each, 1:1H, NH and 2-H); ¹³C{¹H} NMR (CDCl₃, 23 °C) δ 241.42 (Cq, Cr=C), 223.48 and 218.71 (Cq each, 1:4, *trans*- and *cis*-CO, Cr(CO)₅), 144.28 (Cq, C6), 137.30, 137.02 and 134.23 (Cq each, *i*-C of 3 × Ph), 130.60 (C5), 129.65, 129.28, 128.92, 126.22, 126.05, 124.88 and 124.27 (4:1:4:1:2:2:1 CH, 3 × Ph), 73.85 (Cq, C2); IR (KBr) cm⁻¹: 3377(30) [ν (N–H)], 2048 (40), 1911 (70) [ν (C≡O)], 1526 (30), 1492 (30) [ν (C=C)]. Anal. Calc. for C₂₇H₁₈CrN₂O₅: C, 64.54; H, 3.61; N, 5.58. Found: C, 64.52; H, 3.77; N, 5.44%.

*4.15. Synthesis of 4-(1,1,1,1,1-pentacarbonyl-1-tungsta)-1,2,6-triphenyl-1,2,3,4-tetrahydropyrimidine (**26b**)*
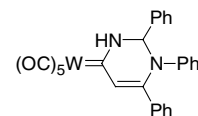
In a fashion similar to synthesis of **26a**, 0.5 mmol of **25b** reacted with NaBH₄ (0.5 mmol) in THF afforded **26b** as orange crystals (191 mg, 60.3%). Single crystals were obtained by recrystallization from dichloromethane/pentane at −20 °C. M.p.: 154 °C; ¹H NMR (CDCl₃, 23 °C, 400 MHz) δ 8.14 (s, 1H, 5-H), 7.70, 7.59, 7.55–7.42, 7.39–7.28, 7.19 and 7.09 (m each, 2:2:3:5:1:3H, NH and 3 × Ph), 6.25 (s, 1H, 2-H); ¹³C{¹H} NMR (CDCl₃, 23 °C) δ 219.97 (s, Cq, W=C), 203.68 and 199.36 (Cq each, 1:4,

trans- and *cis*-CO, W(CO)$_5$), 144.29 (Cq, C6), 139.95, 137.14 and 134.03 (Cq each, *i*-C of 3 × Ph), 130.71 (C5), 129.69, 129.54, 129.34, 128.94, 126.53, 126.26, 126.12, 124.87 (2:2:1:4:1:1:2:2 CH, 3 × Ph), 74.26 (Cq, C2); IR (KBr) cm^{-1}: 3373 (45) [v (N–H)], 2056 (65), 1907 (95) [v (C≡O)], 1527 (55), 1491 (55), 1446 (45) [v (C=C)]. Anal. Calc. for C$_{27}$H$_{18}$N$_2$O$_5$W: C, 51.13; H, 2.86; N, 4.42. Found: C, 51.26; H, 3.02; N, 4.26%.

4.16. Synthesis of Pentacarbonyl(1,2,6-triphenyl-1H-pyrimidine-4-thione)chromium (27a)
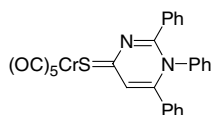
Powdered sulfur (32 mg, 1.0 mmol) and sodium borohydride (38 mg, 1.0 mmol) were added to a solution of ethanol (10 mL), and the mixture was vigorously stirred at ambient temperature for 1 h under nitrogen atmosphere. Complex **25a** (250 mg, 0.5 mmol) was then added in one portion under a nitrogen atmosphere, and the reaction was monitored by TLC on silica gel. After **25a** was completely consumed over a period of 1 h, all the volatiles were removed under reduced pressure. The resultant residue was purified by flash silica gel column chromatography (v/v, hexanes/CH$_2$Cl$_2$ = 1:1) afforded **27a** as dark red crystals (180 mg, 67.7%). Single crystals were obtained by recrystallization from CH$_2$Cl$_2$/pentane at −20 °C. M.p.: 148 °C (dec.); ^{1}H NMR (CDCl$_3$, 23 °C, 400 MHz) δ 7.52 (s, 1H, 5-H), 7.41, 7.35, 7.28, 7.20, 7.09, and 6.91 (m each, 2:2:5:2:2:2H, 3 × Ph); ^{13}C{^{1}H} NMR (CDCl$_3$, 23 °C) δ 224.81 and 217.05 (Cq each, 1:4, *trans-* and *cis*-CO, Cr(CO)$_5$), 196.69 (Cq, S=C), 156.96 and 146.94 (Cq each, C2 and C6), 138.05, 133.17 and 131.92 (Cq each, *i*-C of 3 × Ph), 130.60, 130.14, 129.69, 129.56, 129.42, 129.00, 128.89, 128.69 and 128.20 (1:1:2:1:2:2:2:2:2 CH, 3 × Ph), 124.66 (C5); IR (KBr) cm^{-1}: 2054 (45), 1936 (80), 1889 (75) [v (C≡O)], 1587 (90) [v (C=N)], 1585 (60), 1511 (35), 1481 (35) [v (C=C)], 1334 (35) [v (S=C)]. Anal. Calc. for C$_{27}$H$_{16}$CrN$_2$O$_5$S: C, 60.90; H, 3.03; N, 5.26. Found: C, 60.94; H, 2.96; N, 5.00%.

4.17. Synthesis of Pentacarbonyl(1,2,6-triphenyl-1H-pyrimidine-4-thione)tungsten (27b)
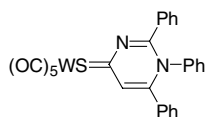
In a fashion similar to synthesis of **27a**, 0.5 mmol of **25b** reacted with NaBH$_4$ and S$_8$ (1.0 mmol each) in ethanol afforded **27b** as dark red crystals (295 mg, 88.7%). Single crystals were obtained by recrystallization from CH$_2$Cl$_2$/pentane at −20 °C. M.p.: 163–164 °C (dec.); ^{1}H NMR (CDCl$_3$, 23 °C, 400 MHz) δ 7.56 (s, 1H, 5-H), 7.38–7.33, 7.29–7.24, 7.23–7.15, 7.09 and 6.91 (m each, 4:4:3:2:2H,

3 × Ph); ^{13}C{^{1}H} NMR (CDCl$_3$, 23 °C) δ 203.44 and 198.58 (Cq each, 1:4, *trans-* and *cis*-CO, W(CO)$_5$), 194.95 (Cq, S=C), 157.47 and 148.40 (Cq each, C2 and C6), 137.92, 133.00 and 131.76 (Cq each, *i*-C of 3 × Ph), 130.65, 130.27, 129.66, 129.47, 128.96, 128.80, 128.74, 128.23 (CH of 3 × Ph), 124.05 (C5); IR (KBr) cm^{-1}: 2060 (70), 1929 (95), 1876 (95) [v (C≡O)], 1587 (80) [v (C=N)], 1570 (65), 1481 (60) [v (C=C)], 1333 (60) [v (S=C)]. Anal. Calc. for C$_{27}$H$_{16}$N$_2$O$_5$SW: C, 48.81; H, 2.43; N, 4.22. Found: C, 48.88; H, 2.55; N, 4.03%.

4.18. Synthesis of Pentacarbonyl(1,2,6-triphenyl-1H-pyrimidine-4-selone)chromium (28a) and 1,2,6-triphenyl-1H-pyrimidine-4-selone (29)
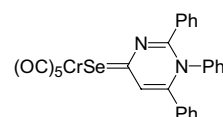
A mixture of elemental selenium (79 mg, 1.0 mmol) and sodium borohydride (38 mg, 1.0 mmol) in ethanol (10 mL) was vigorously stirred at ambient temperature for 1 h under nitrogen atmosphere. Complex **25a** (250 mg, 0.5 mmol) was then added in one portion and the reaction was monitored by TLC on silica gel. After **25a** was completely consumed over a period of 1 h, all the volatiles were removed under reduced pressure. The resultant residue was purified by flash silica gel column chromatography (v/v, hexanes/CH$_2$Cl$_2$ = 1:1) afforded **28a** as dark brown crystals (71 mg, 24.6%) and **29** (v/v, dichloromethane/diethyl ether = 1:1) as red crystals (136 mg, 70.4%), respectively. **28a**: Single crystals were obtained from recrystallization in dichloromethane and pentane at −20 °C. M.p. 134–136 °C (dec.); ^{1}H NMR (CDCl$_3$, 23 °C, 400 MHz) δ 7.86 (s, 1H, 5-H), 7.42–7.10 and 6.92 (m each, 13:2 H, 3 × Ph); ^{13}C{^{1}H} NMR (CDCl$_3$, 23 °C) δ 225.75 and 217.98 (s and Cq each, 1:4, *trans-* and *cis*-CO, Cr(CO)$_5$), 197.69 (s, Cq, Se=C), 155.88 and 146.25 (s and Cq each, C2 and C6), 138.04, 132.93 and 131.74 (s and Cq each, *i*-C of 3 × Ph), 130.70, 130.26, 129.71, 129.48, 128.74, 128.63, 128.37 and 128.23 (s each, 1:1:3:2:2:2:2:2 CH of 3 × Ph); IR (KBr) cm^{-1}: 2048 (65), 1934 (90), 1887 (85) [v (C≡O)], 1585 (65) [v (C=N)], 1477 (50) [v (C=C)], 1327 (50) [v (Se=C)]. Anal. Calc. for C$_{27}$H$_{16}$CrN$_2$O$_5$Se: C, 55.97; H, 2.78; N, 4.84. Found: C, 56.10; H, 2.70; N, 4.62%.

4.19. 1,2,6-Triphenyl-1H-pyrimidine-4-selone (29)
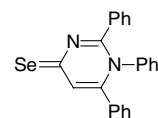
Red crystals (136 mg, 70.4% from **25a**; 90 mg, 46.6% from **25b**). Single crystals suitable for X-ray crystallographic study were obtained by recrystallization from

CH$_2$Cl$_2$/pentane at −20 °C. M.p.: 252–254 °C; ^{1}H NMR (CDCl$_3$, 23 °C, 400 MHz) δ 7.79 (s, 1H, 5-H), 7.37, 7.34–7.06, and 6.91 (m each, 2:11:2H, 3 × Ph); ^{13}C{^{1}H} NMR (CDCl$_3$, 23 °C) δ 201.13 (Cq, Se=C), 154.50 and 146.17 (Cq each, C2 and C6), 138.48, 133.83 and 129.35 (Cq each, *i*-C of 3 × Ph), 132.26 (C5), 130.08, 129.76, 129.70, 129.26, 129.19, 128.61, 128.53, 128.45 and 127.96 (1:1:2:1:2:2:2:2:2 CH, 3 × Ph); IR (KBr) cm^{-1}: 1570 (60) [ν (C=N)], 1479 (50) [ν (C=C)], 1093 (50), [ν (Se=C)]. Anal. Calc. for C$_{22}$H$_{16}$N$_2$Se: C, 68.22; H, 4.16; N, 7.23. Found: C, 67.75; H, 4.36; N, 7.04%.

4.20. Synthesis of pentacarbonyl(1,2,6-triphenyl-1H-pyrimidine-4-selone)tungsten (28b) and (29)
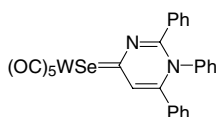
In a fashion similar to synthesis of **28a** and **29**, 0.5 mmol of **25b** reacted with NaBH$_4$ and Se (1.0 mmol each) in ethanol afforded **28b** as dark brown crystals (186 mg, 52.3%). Single crystals were obtained by recrystallization from CH$_2$Cl$_2$/pentane at −20 °C. M.p.: 164 °C (dec.); ^{1}H NMR (CDCl$_3$, 23 °C, 400 MHz) δ 7.91 (s, 1H, 5-H), 7.38–7.35, 7.29–7.15, 7.09, and 6.92 (m each, 4:7:2:2H, 3 × Ph); ^{13}C{^{1}H} NMR (CDCl$_3$, 23 °C) δ 203.57 and 198.98 (Cq each, 1:4, *trans*- and *cis*-CO, W(CO)$_5$), 196.54 (Cq, Se=C), 156.32 and 147.45 (Cq each, C2 and C6), 137.99, 132.82 and 131.66 (Cq each, *i*-C of 3 × Ph), 130.77, 130.38, 129.81, 129.72, 129.53, 128.80, 128.66, 128.39, and 128.28 (1:1:1:2:2:2:2:2:3 CH, 3 × Ph); IR (KBr) cm^{-1}: 2058 (25), 1930 (45), 1879 (40) [ν (C≡O)], 1585 (30) [ν (C=N)], 1479 (25) [ν (C=C)], 1327 (20) [ν (Se=C)]. Anal. Calc. for C$_{27}$H$_{16}$N$_2$O$_5$SeW: C, 45.60; H, 2.27; N, 3.94. Found: C, 45.84; H, 2.38; N, 3.80%. From the same reaction, **29** (90 mg, 46.6%) was isolated.

4.21. X-ray crystallographic studies

Single crystal X-ray diffraction studies for complexes **25b**, **28b**, and pyrimidine-selone **29** were carried out on a SMART APEX diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Cell parameters were obtained by global refinement of the positions of all collected reflections. Intensities were corrected for Lorentz and polarization effects and empirical absorption. The structures were solved by direct methods and refined by full-matrix least-squares on F^2. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in calculated positions. Structure solution and refinement were performed by using the SHELXL-97 package. Crystal data and refinement details for these compounds are summarized in Table 2.

Appendix A. Supporting data

The X-ray crystallographic files, in CIF format, are available from the Cambridge Crystallographic Data Centre on quoting the deposition numbers: CCDC 602802 for **25b**, CCDC 602804 for **28b**, and CCDC 602803 for **29**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 IEZ, UK, fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.05.021.

References

[1] (a) For selected recent reviews, see: J. Barluenga, J. Santamaria, M. Tomás, Chem. Rev. 104 (2004) 2259;
(b) J.W. Herndon, Coord. Chem. Rev. 243 (2003) 3;
(c) M.A. Sierra, Chem. Rev. 100 (2000) 3591;
(d) K.H. Dötz, C. Jakel, W.C. Haase, J. Organomet. Chem. 617/618 (2001) 119;
(e) J. Barluenga, J. Floréz, F.J. Fañanás, J. Organomet. Chem. 624 (2001) 5;
(f) A. de Meijere, H. Schirmer, M. Duetsch, Angew. Chem., Int. Ed. Engl. 39 (2000) 3964;
(g) J.W. Herndon, Tetrahedron 56 (2000) 1257;
(h) J. Barluenga, F.J. Fañanás, Tetrahedron 56 (2000) 4597;
(i) R. Aumann, Eur. J. Org. Chem. 1 (2000) 17.
[2] J.Z. Chen, Z.K. Yu, Z.Y. Zheng, K.C. Gu, S.Z. Wu, F.L. Zeng, W.Q. Tan, X.W. Wu, W.-J. Xiao, Organometallics 24 (2005) 302, and references therein.
[3] (a) J. Barluenga, F. Aznar, I. Gutiérrez, A. Martín, S. García-Granda, M.A. Llorca-Baragaño, J. Am. Chem. Soc. 122 (2000) 1314;
(b) K.H. Dötz, Angew. Chem., Int. Ed. Engl. 14 (1975) 644.
[4] (a) K.H. Dötz, Angew. Chem., Int. Ed. Engl. 14 (1975) 644;
(b) J. Barluenga, F. Aznar, I. Gutiérrez, A. Martín, S. García-Granda, M.A. Llorca-Baragaño, J. Am. Chem. Soc. 122 (2000) 1314;
(c) S. Florio, F.M. Perna, R. Luisi, J. Barluenga, F.J. Fañanás, F. Rodríguez, J. Org. Chem. 69 (2004) 9204, and references therein.
[5] (a) Representative references: L.S. Hegedus, Tetrahedron 53 (1997) 4105;
(b) L.S. Hegedus, Transition metal carbene complexes: photochemical reactions of carbene complexes, in: E.W. Abel, F.G.A. Stone, G. Wilkinson (Eds.), Comprehensive Organometallic Chemistry II, vol. 12, Pergamon, Oxford, 1995, p. 549.
[6] (a) M. Gómez-Gallego, M.J. Mancheño, M.A. Sierra, Acc. Chem. Res. 38 (2005) 44;
(b) J. Barluenga, P. Barrio, R. Vicente, L.A. López, M. Tomás, J. Organomet. Chem. 689 (2004) 3793.
[7] (a) J. Barluenga, F. Aznar, A. Martin, S. García-Granda, E. Pérez-Carreño, J. Am. Chem. Soc. 116 (1994) 11191;
(b) W.D. Wulff, B.M. Bax, T.A. Brandvold, K.S. Chan, A.M. Gilbert, R.P. Hsung, J. Mitchell, J. Clardy, Organometallics 13 (1994) 102.
[8] (a) P. Ramírz-López, M.A. Sierra, M. Gómez-Gallego M.J. Mancheño, H. Gornitzka, Organometallics 22 (2003) 5092;
(b) P. Ramírz-López, M. Gómez-Gallego, M.J. Mancheño, M.A. Sierra, M. Bilurbina, S. Ricart, J. Org. Chem. 68 (2003) 3538;

(c) M. Gómez-Gallego, M.J. Mancheño, P. Ramírez, C. Piñar, M.A. Sierra, Tetrahedron 56 (2000) 4893;

(d) J. Barluenga, A. Granados, F. Rodríguez, J. Vadecard, F.J. Fañanás, Tetrahedron Lett. 38 (1997) 6465.

[9] (a) Selected references see: W.D. Wulff, W.E. Bauta, R.W. Kaesler, P.J. Lankford, R.A. Miller, C.K. Murray, D.C. Yang, J. Am. Chem. Soc. 112 (1990) 3642;

(b) J. Barluenga, F. Aznar, S. Barluenga, M. Fernández, A. Martin, S. García-Granda, A. Pinera-Nicolas, Chem. Eur. J. 4 (1998) 2280;

(c) M.A. Vázquez, L. Reyes, R. Miranda, J.J. García, H.A. Jiménez-Vázquez, J. Tamariz, F. Delgado, Organometallics 24 (2005) 3413.

[10] (a) For selected recent literatures, see: B. Alcaide, L. Casarrubias, G. Domínguez, M.A. Sierra, Curr. Org. Chem. 2 (1998) 551;

(b) J. Barluenga, M.A. Fernández-Rodríguez, E. Aguilar, F. Fernández-Marí, B. Olano, A. Salinas, Chem. Eur. J. 7 (2001) 3533.

[11] (a) I. Merino, Y.R.S. Laxmi, J. Flórez, J. Barluenga, J. Ezquerra, C. Pedregal, J. Org. Chem. 67 (2002) 648;

(b) K.C. Gu, J.Z. Chen, Z.Y. Zheng, S.Z. Wu, X.W. Wu, X.W. Han, Z.K. Yu, Polyhedron 24 (2005) 173, and references therein.

[12] (a) B.A. Anderson, W.D. Wulff, A. Rham, J. Am. Chem. Soc. 115 (1993) 4602;

(b) W.D. Wulff, D.C. Yang, J. Am. Chem. Soc. 105 (1983) 6726;

(c) E.O. Fischer, S. Walz, G. Kneis, F.R. Kreissl, Chem. Ber. 110 (1977) 1651.

[13] E.O. Fischer, D. Plabst, Chem. Ber. 107 (1974) 3326.

[14] C.P. Casey, S.H. Betz, T.J. Burkhardt, Tetrahedron Lett. 14 (1973) 1421.

[15] C.P. Casey, T.J. Burkhardt, J. Am. Chem. Soc. 94 (1972) 6543.

[16] J. Barluenga Jr., P.L. Bernard, J.M. Concellón, Tetrahedron Lett. 35 (1994) 9471.

[17] C.P. Casey, M. Neumann, J. Am. Chem. Soc. 99 (1977) 1651.

[18] (a) Selected references, see: F.A. Cotton, C.M. Lukehart, J. Am. Chem. Soc. 93 (1971) 2672;

(b) G. Erker, F. Sosna, Organometallics 9 (1990) 1949;

(c) P. Quayle, S. Rahman, E.L.M. Ward, J. Herbert, Tetrahedron Lett. 35 (1994) 3801;

(d) J. Barluenga, M. Tomás, J.A. López-Pelegrín, E. Rubio, Tetrahedron Lett. 38 (1997) 3981;

(e) J. Ezquerra, C. Pedregal, I. Merino, J. Flórez, J. Barluenga, S. García-Granda, M.-A. Llorca, J. Org. Chem. 64 (1999) 6554;

(f) J. Barluenga, M.A. Fernández-Rodríguez, E. Aguilar, Org. Lett. 4 (2002) 3659;

(g) V. Capriati, S. Florio, R. Luisi, F.M. Perna, J. Barluenga, J. Org. Chem. 70 (2005) 5852.

[19] (a) C.P. Casey, T.J. Burkhardt, C.A. Bunnell, J.C. Calabrese, J. Am. Chem. Soc. 99 (1977) 2127;

(b) K.S. Chan, M.L. Yeung, W. Chan, R. Wang, T.C.W. Mak, J. Org. Chem. 60 (1995) 1741.

[20] (a) M. Gibert, M. Ferrer, A.-M. Lluch, F. Sanchez-Baeza, A. Messeguer, J. Org. Chem. 64 (1999) 1591;

(b) A.-M. Lluch, M. Gibert, F. Sánchez-Baeza, A. Messeguer, Tetrahedron 52 (1996) 3973.

[21] (a) C.P. Casey, R.A. Boggs, R.L. Anderson, J. Am. Chem. Soc. 94 (1972) 8947;

(b) C.P. Casey, W.R. Brunsvold, J. Organomet. Chem. 102 (1975) 175;

(c) R. Neidlein, S. Gurtler, Synthesis (1995) 325.

[22] C.M. Lukehart, J.V. Zeile, J. Organomet. Chem. 97 (1975) 421.

[23] (a) R. Aumann, J. Schroeder, H. Heinen, Chem. Ber. 123 (1990) 1369;

(b) E. Licandro, S. Maiorana, A. Papagni, P. Hellier, L. Capella, A. Persoons, S. Houbrechts, J. Organomet. Chem. 583 (1999) 111;

(c) J. Barluenga, F. Andina, M.A. Fernández-Rodríguez, P. Garcia-García, I. Merino, E. Aguilar, J. Org. Chem. 69 (2004) 7352.

[24] D. Perdicchia, E. Licandro, S. Maiorana, B. Vandoni, C. Baldoli, Org. Lett. 4 (2002) 827.

[25] K.H. Dötz, B. Fügen-Köster, D. Neugebauer, J. Organomet. Chem. 182 (1979) 489.

[26] R.L. Beddoes, J.E. Painter, P. Quayle, Tetrahedron Lett. 37 (1996) 9385.

[27] J. Barluenga, A. Ballesteros, R.B. de la Rúa, J. Santamaría, E. Rubio, M. Tomás, J. Am. Chem. Soc. 125 (2003) 1834.

[28] R. Aumann, Z.K. Yu, R. Fröhlich, Organometallics 17 (1998) 2897.

[29] (a) E.O. Fischer, S. Riedmüller, Chem. Ber. 107 (1974) 915;

(b) A.R. Shah, D.K. Padma, A.R.V. Murthy, Indian J. Chem. 9 (1971) 885.

[30] (a) Selected literatures, see: A. Couture, P. Grandclaudon, E. Huguerre, Synthesis (1989) 456;

(b) H. Fischer, K. Treier, C. Troll, Chem. Ber. 128 (1995) 883;

(c) W.H. Bunnelle, B.R. Mckinnis, B.A. Narayanan, J. Org. Chem. 55 (1990) 768;

(d) T. Murai, Y. Ogino, T. Mizutani, T. Kanda, S. Kato, J. Org. Chem. 60 (1995) 2942;

(e) D.H.R. Barton, P.-E. Hansen, K. Picker, J. Chem. Soc. Perkin I (1977) 1723.

[31] E.O. Fischer, F.R. Kreissl, J. Organoment. Chem. 35 (1972) C47.

[32] R. Aumann, H. Heinen, Chem. Ber. 120 (1987) 537.

[33] (a) R. Aumann, E.O. Fischer, Angew. Chem., Int. Ed. Engl. 6 (1967) 879;

(b) M.Y. Darensbourg, D.J. Darensbourg, Inorg. Chem. 9 (1970) 32.

[34] S.K. Kang, S.K. Yoon, Y.M. Kim, Org. Lett. 3 (2001) 2697.

[35] V. Balasubramaniyan, G. Bhatia, S.B. Wagh, Tetrahedron 39 (1983) 1475.

[36] F.D. Lewis, D.K. Howard, S.V. Barancyk, J.D. Oxman, J. Am. Chem. Soc. 108 (1986) 3016.

[37] F.D. Lewis, D.K. Howard, J.D. Oxman, A.L. Upthagrove, S.L. Quillen, J. Am. Chem. Soc. 108 (1986) 5964.

[38] Z.J. Shi, C. He, J. Org. Chem. 69 (2004) 3669.

[39] (a) W.J. Tao, S. Nesbitt, R.F. Heck, J. Org. Chem. 55 (1990) 63;

(b) M.J. Dai, B. Liang, C.H. Wang, J.H. Chen, Z. Yang, Org. Lett. 6 (2004) 221.