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Synthesis of chromium *N*-heterocyclic carbene complexes using chromium Fischer carbenes as a source of chromium carbonyls

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Abstract

Chromium Fischer carbene complexes, $[Cr\{=OMe(R)\}(CO)_5]$ have been utilized as a source of chromium carbonyls in the synthesis of chromium NHC complexes. Using the synthetic method, chromium complexes of various NHC ligands were isolated in reasonable yields. Moreover, the method can be employed for the synthesis of molybdenum and tungsten NHC compounds.
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1. Introduction

N-heterocyclic carbene (NHC) ligands have recently become very popular as an alternative to phosphines [1]. Stable NHCs, in particular, display rich coordination chemistry and have found a multitude of applications as catalyst components due to their remarkable ligand properties [2]. Thus, synthetic efforts towards transition metal complexes containing NHCs have been the subject of intense interest. Methods for synthesizing these complexes mainly consist of direct reaction of either the stable Arduengo's carbene or the imidazolium salt with appropriate metal fragments, and via four-component condensation reactions with cyano transition metal complexes [3]. Very recently, Crabtree et al. reported on the use of imidazolium-2-carboxylates as efficient precursors to NHC complexes of Rh, Ru, Ir, and Pd [4].

Amongst Fischer carbenes, the chromium metal compound is one of the most studied metal compounds. However, although the first chromium NHC complex was reported 38 years ago by Öfele [5], the chemistry of chromium NHC complexes has not been well developed, presumably in part due to the lack of generally applicable synthetic procedures. Thus, studies on the synthesis of chromium NHC complexes exist in only a handful of examples. Most of the reported methods [6] used $Cr(CO)_6$, $Cr(CO)_5(THF)$, and $Na_2Cr_2(CO)_{10}$ as chromium carbonyl sources. They reacted directly with NHCs. Sometimes reasonable yields were obtained, but sometimes the yields were poor. Thus, the NHCs studied were limited to some specific substrates. Recently, Hahn et al. reported [7a,7b] a template synthesis of chromium benzanulated NHC complexes. A similar reaction was also reported by Michelin et al. [7c] Öfele et al. reported the synthesis of tetrazole and triazole NHC complexes of group six carbonyls [8]. The development of new methodologies towards preparation of chromium NHC complexes remains an important synthetic endeavor.

Recently, we attempted to synthesize a chromium complex containing a Fischer carbene and an NHC ligand by the reaction of $[Cr\{=OMe(R)\}(CO)_5]$ with NHC.

Surprisingly, a chromium NHC complex was obtained as the sole chromium product. The chromium Fischer carbene acted as a source of chromium carbonyls. Herein we wish to communicate our preliminary results for the synthesis of chromium NHC complexes via a reaction of chromium Fischer carbenes with NHCs and an X-ray crystal structure of one of them. Moreover, the method can be employed for the synthesis of molybdenum and tungsten NHC complexes.

2. Results and discussion

We first screened the reaction conditions to find an efficient and general method for the synthesis of chromium NHC complexes using $[Cr\{=OMe(R)\}(CO)_5]$ (R = Me, n-Bu, Ph) as a chromium carbonyl source, and also screened chromium carbonyl sources, such as $Cr(CO)_6$ and $Cr(THF)(CO)_5$ in order to make a comparison (Table 1).

An NHC ligand, N,N'-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (I-Pr), **1A**, was used as a model ligand. The use of $[Cr\{=OMe(R)\}(CO)_5]$ (R = Me, n-Bu, Ph) as a chromium carbonyl source in the synthesis of chromium NHC complexes has never been reported. However, the nucleophilic substitution of the carbene ligand in chromium Fischer carbenes is already well known [9]. The formation of a chromium NHC complex, **2A**, was confirmed by NMR, IR, elemental analyses, and an X-ray diffraction study (Fig. 1) [10,11]. The ^{13}C NMR spectrum of **2A** reveals the signal of the carbene C atom at δ 199.9, lying in a typical range of the chromium compounds with unsaturated NHCs [6a]. Other spectroscopic data for **2A** are in line with its proposed structure [6]. One notable thing in the X-ray crystal structure of **2A** is that the NHC ligand is eclipsed to the equatorial chromium tetracarbonyl and
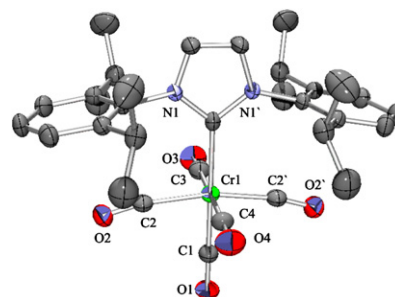

Fig. 1. Crystal structure of **2A** (30% thermal ellipsoid).

the eclipsed carbonyls are highly bent ($\angle Cr1–C2–O2 = 169.4(2)°$) compared to other carbonyls (av. $\angle Cr–C–O = 176.4°$) [10]. The yield of the reaction was highly dependent upon the reaction temperature (entries **1**–**3** and **4**–**6**), slightly dependent upon the reaction medium (entries **2** and **5**), and was rather insensitive to the chromium Fischer carbenes (entries **6**–**8**). At room temperature, no reaction (entries **1** and **4**) was observed. However, as the reaction temperature increased, the yield increased to 62–63% (entries **6**–**8**) in THF solution. When $Cr(CO)_6$ or $Cr(THF)(CO)_5$ was used as a source of chromium carbonyl, poor yields (entries **9**–**10**) were obtained. Thus, the following reaction conditions were employed to study other reactions: 1.0 equiv $[Cr\{=OMe(Ph)\}(CO)_5]$, 1.2 equiv NHC, THF, 70 °C (the temperature of the reaction bath), and for 2 h. Table 2 summarizes the reaction of $[Cr\{=OMe(Ph)\}(CO)_5]$ with various NHC ligands [11].

Table 1
Screening of chromium source[a]

I-Pr = 2,6-diisopropylphenyl

Entry	Cr complex (L)	Solvent	T (°C)	Yield[b]
1		Toluene	r.t.	N.R.
2		Toluene	50	38
3	:C(OMe)Ph	Toluene	Reflux	53
4		THF	r.t.	N.R.
5		THF	50	41
6		THF	Reflux	62
7	:C(OMe)Bu	THF	Reflux	63
8	:C(OMe)Me	THF	Reflux	63
9	THF	THF	Reflux	Trace
10	CO	THF	Reflux	16

[a] Reaction conditions: 0.12 mmol imidazolium salt, 4 ml solvent, 0.13 mmol KO^{t}Bu and 0.10 mmol chromium source.
[b] Isolated yield.

Table 2
Synthesis of various chromium NHC complexes[a]

X = Cl, Br, I, PF$_6$
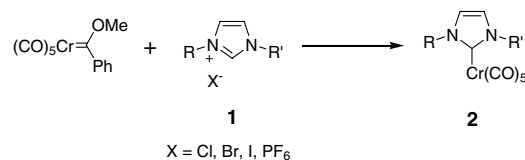
Entry	Imidazolium salt (**1**)		Product (**2**)	Yield (%)[b]
1	R,R′ = 2,6-diisopropylphenyl (I-Pr)	**1A**	**2A**	62
2	R,R′ = mesityl (Mes)	**1B**	**2B**	67
3	R,R′ = 2,6-dimethylphhenyl	**1C**	**2C**	57
4	R,R′ = 4-bromo-2,6-dimethylphhenyl	**1D**	**2D**	66
5	R = phenyl (Ph), R′ = methyl (Me)	**1E**	**2E**	50
6	R = Ph, R′ = n-Bu	**1F**	**2F**	66
7	R = Ph, R′ = Benzyl (Bn)	**1G**	**2G**	46
8	R,R′ = Bn	**1H**	**2H**	34
9	R = Bn, R′ = i-Bu	**1I**	**2I**	35
10	R = n-Bu, R′ = Me	**1J**	**2J**	48
11[c]	R,R′ = Me	**1K**	**2K**	29
12[d]	R,R′ = 2,6-dimethylphenyl	**1C**	**2C**	42
13[d,e]	R,R′ = 2,6-dimethylphenyl	**1C**	**2C**	24

[a] Reaction conditions: 0.38 mmol imidazolium salt, 10 ml thf, 0.42 mmol KO^{t}Bu, 0.32 mmol chromium Fisher carbene, 70 °C, 2 h.
[b] Isolated yield.
[c] Reaction temperature: room temperature.
[d] Microwave irradiation, 80 °C, 10 min.
[e] Cr(Co)$_6$ used.

Under optimized reaction conditions, **2B** was obtained in 67% yield from **1B**. In the same way, **2C** and **2D** were obtained in 57% and 66% yields, respectively. Recently, microwave radiation has been widely used as a source of energy [12]. When microwaves are used as a source of energy, the reaction time can be shortened and, in some cases, much higher yields than those obtained in the conventional thermal reactions have been achieved [13]. Thus, we studied a reaction of **1C** with [Cr{=OMe(Ph)}(CO)$_5$] or Cr(CO)$_6$ under irradiation of microwave (at 80 °C for 10 min; entries 12 and 13). After work-up, **2C** was obtained in 42% and 24% yields, respectively. The microwave irradiation was not helpful for the synthesis of **2C**. From **1E**, **1F**, and **1G** compounds **2E**, **2F**, and **2G** were obtained in 50%, 66%, and 46% yields, respectively. When all the substituents on the NHC were an alkyl group, the yields were rather poor: compounds **2H–2K** were obtained in rather poor yields, 34%, 35%, 48%, and 29% yields, respectively, from **1H–1K**. The yield of the reaction was dependent upon the substituent(s) on the NHC: as the number of the aryl substituent on the NHC increased, the yield increased. This observation might be related to the stability of the NHC anion under the reaction conditions [14].

The chromium Fischer carbene was also used as the chromium carbonyl source in the synthesis of chromium benzimidazolin-2-ylidene complexes (Table 3) [11]. Although the yields of the reactions were not good enough, the result demonstrated that the chromium Fischer carbene was much better than Cr(CO)$_6$ as a source of chromium carbonyl in the synthesis of chromium NHC complexes.

Employing the same reaction for the synthesis of a chromium triad afforded molybdenum and tungsten compounds (**3A** and **4A**) in 91% and 40% yields, respectively (Scheme 1). The reason why there is a big difference in the yields is not clear [15]. When Mo(CO)$_6$ and W(CO)$_6$ were used instead of chromium Fischer carbene, **3A** and **4A** were obtained in 32% and 21% yields, respectively. Recently, **3A** was prepared in 67% yield by a reaction of Mo(CO)$_6$ with triethylborane adduct of *N*-heterocyclic carbine [16].
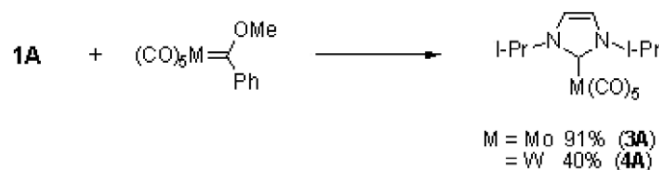
Scheme 1. Synthesis of molbdenum and tungsten NHC complexes.

Scheme 2. Reaction of [(CO)$_5$Cr(PPh$_3$)] and NHC in progression, react with PPh$_3$.

To synthesize a chromium complex having a phosphine and an NHC ligand, triphenyl-phospine (pentacarbonyl)chromium was treated with an NHC ligand. Interestingly, an NHC-substituted chromium carbonyl compound was obtained in 44% yield (Scheme 2). Thus, instead of carbonyl, triphenylphosphine was replaced by the NHC. A similar substitution reaction was reported for a reaction of V(CO)$_5$PR$_3^-$ (R = Ph, *n* − Bu) with P(OPh)$_3$ [17]. Thus, in order to make a chromium complex having a phosphine and an NHC ligand, the reaction route changed to react (NHC)Cr(CO)$_5$ with PPh$_3$. However, the formation of a chromium complex bearing NHC and phosphine was not observed.

3. Conclusions

In conclusion, we have developed a new synthetic method for producing chromium complexes with NHC ligands via a reaction of chromium Fischer carbenes with NHC ligands. We found a correlation between the yield of the reaction and the substituent(s) on the NHC for a series of chromium NHC complexes. We expect that our synthetic study will boost the study of the chemistry of chromium NHC complexes in the near future.

4. Experimental

General. Thin-layer chromatography (TLC) was performed on 0.25 mm Merck silica gel coated plates treated with a UV (254 nm). TLC plates were visualized by ultraviolet light. THF was purified by distillation from sodium/benzophenone under nitrogen and toluene was distilled from sodium under nitrogen. Reagents were purchased from Aldrich Chemical Co. and Strem Chemical Co. and were used as received. All yields are based upon isolated materials. ^{1}H and ^{13}C NMR spectra were obtained with a Bruker 300 MHz spectrometer. Coupling constants (*J* values) are reported in hertz (Hz), and spin multiplicities are indicated by the following symbols: s (singlet), d (doublet), t (triplet), q (quartet), and m (multiplet). Melting points were obtained with a MEL-TEMP II (Laboratory

Table 3
Synthesis of chromium benzimidazolin-2-ylidene complexes using chromium Fischer carbene[a]

	2L (R = Me)	**2M** (R = *n*-Bu)	**2N** (R = Bn)
Yield (%)	42	44	42
Yield (%)[b]	16	Trace	N.R.

[a] Reaction conditions: 0.38 mmol imidazolium salt, 10 ml thf, 0.42 mmol KO^{t}Bu 0.32 mmol chromium Fisher carbene, 70 °C, 2 h.
[b] Cr(Co)$_6$ used.

Devices). Infrared spectra were recorded on a Shimadzu IR-470 spectrometer. IR spectra were obtained as films on NaCl by evaporation of solvent or in $CHCl_3$ solution. Infrared spectra band positions are reported in reciprocal centimeters (cm^{-1}). Elemental analyses were done at the National Center for Inter-University Research Facilities, Seoul National University. High-resolution mass spectra were obtained at Korea Basic Science Institute (Daegu, Korea). High-resolution mass spectral (HRMS) data are reported in the form of m/z (intensity relative to base peak = 100). Flash chromatography was performed using Merck Silica Gel 60 (230–400 mesh).

5. Representative procedure for the synthesis of chromium NHC (2A)

To a flame-dried 50 ml schlenk flask, imidazolium salt (**1A**, 0.38 mmol), KO^tBu (0.42 mmol), and THF (10 ml) were added. After the solution was stirred at room temperature for 0.5 h, 0.32 mmol chromium Fischer carbene was added in one portion. The reaction temperature was raised to 70 °C. After the solution was stirred for 2 h, the mixture was cooled to room temperature. After the solvent was removed under reduced pressure, a flash column chromatography on a silica gel eluting with hexane and diethyl ether (v/v, 10:1) gave the product (**2A**). Suitable single crystals of **2A** for an X-ray diffraction study were grown by slow evaporation of an ether solution of **2A** at −15 °C. ^1H NMR ($CDCl_3$, 300 MHz): 1.13 (d, $J = 6.9$ Hz, 12 H), 1.37 (d, $J = 6.9$ Hz, 12 H), 2.68 (m, 4 H), 7.09 (s, 2 H), 7.33 (d, $J = 7.8$ Hz, 4 H), 7.51 (t, $J = 7.8$ Hz, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz): 22.8, 26.2, 28.8, 124.5, 125.7, 130.9, 137.7, 146.5, 199.9, 216.1, 221.1; IR ν_{CO} ($CHCl_3$): 1919.2 cm^{-1}, 2048.0 cm^{-1}. Exact mass for $C_{32}H_{36}N_2O_5Cr_1$, FAB: Calc. 580.2029. Found. 580.2025. Elemental Anal. Calc. for $C_{32}H_{36}N_2O_5Cr_1$: C, 66.18; H, 6.25; N, 4.83. Found. C, 66.52; H, 6.33; N 4.66%. Melting point: 198 °C.

Acknowledgements

Appendix A. Supplementary material

CCDC 290861 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2007.08.043.

References

[1] (a) W.A. Hermann, Angew. Chem., Int. Ed. 41 (2002) 1290;
(b) B.S. Young, S.P. Nolan, Chemtracts 16 (2003) 205.
[2] C.M. Crudden, D.P. Allen, Coord. Chem. Rev. 248 (2004) 2247.
[3] (a) F.E. Hahn, V. Langenhahn, T. Pape, Chem. Commun. (2005) 5390;
(b) F.E. Hahn, V. Langenhahn, T. Lügger, T. Pape, D. Le Van, Angew. Chem., Int., Ed. 44 (2005) 3759;
(c) M. Basato, F. Benetollo, G. Faccin, R.A. Michelin, M. Mozzon, S. Pugliese, P. Sgarbossa, S.M. Sbovata, A. Tassan, J. Organomet. Chem. 689 (2004) 454.
[4] A.M. Voutchkova, L.N. Appelhans, A.R. Chianese, R.H. Crabtree, J. Am. Chem. Soc. 127 (2005) 17624.
[5] K. Öfele, J. Organomet. Chem. 12 (1968) P42.
[6] (a) M. Nonnenmacher, D. Kunz, F. Rominger, T. Oeser, J. Organomet. Chem. 690 (2005) 5647;
(b) C. Bolm, M. Kesselgruber, G. Raabe, Organometallics 21 (2002) 707;
(c) M. Tafipolsky, W. Schere, K. Öfele, G. Artus, B. Pedersen, W.A. Herrmann, G.S. McGrady, J. Am. Chem. Soc. 124 (2002) 5865;
(d) H.G. Raubenheimer, Y. Stander, E.K. Marais, C. Thompson, G.J. Kruger, S. Cronje, M. Deetlefs, J. Organomet. Chem. 590 (1999) 158;
(e) K. Öfele, W.A. Herrmann, D. Mihalios, M. Elison, E. Herdtweck, W. Schere, J. Mink, J. Organomet. Chem. 459 (1993) 177.
[7] (a) F.E. Hahn, C.G. Plumed, M. Münder, T. Lügger, Chem. Eur. J. 10 (2004) 6285;
(b) F.E. Hahn, V. Langenhahn, N. Meier, T. Lügger, W.P. Fehlhammer, Chem. Eur. J. 9 (2003) 704;
(c) M. Basato, G. Facchin, R.A. Michelin, M. Mozzon, S. Pugliese, P. Sgarbossa, A. Tassan, Inorg. Chim. Acta 356 (2003) 349–356.
[8] G.D. Frey, K. Ofele, H.G. Krist, E. Herdtweck, W.A. Herrmann, Inorg. Chim. Acta 359 (2006) 2622.
[9] Recent papers, see M. Ali, S. Gangopadhyay, M. Mijanuddin, J. Organomet. Chem. 690 (2005) 4878;
(b) M. Ali, D. Maiti, J. Organomet. Chem. 689 (2004) 3520;
(c) C.F. Bernasconi, C. Whitesell, R.A. Johnson, Tetrahedron 56 (2000) 4917.
[10] *Crystal data for* **2A**. $C_{32}H_{36}Cr_1N_2O_5$, $M = 580.63$, monoclinic, $a = 9.0001(7)$ Å, $b = 20.0103(10)$ Å, $c = 9.0034(8)$ Å, $\beta = 102.635(3)°$, $U = 1582.2(2)$ Å^3, $T = 293(2)$ K, space group $P21/m$, $Z = 2$. The final R_1 was 0.0615 and $wR(F_2)$ was 0.1057.
[11] Supporting Information Available: Detailed experimental procedures, new characterization data, ^1H and ^{13}C NMR spectra of all compounds.
[12] Recent reviews, see (a) A. de la Hoz, Á. Díaz-Ortiz, A. Moreno, Chem. Soc. Rev. 34 (2005) 164;
(b) B.L. Hayes, Aldrichim. Acta 37 (2004) 66;
(c) H.E. Blackwell, Org. Biomol. Chem. 1 (2003) 1251;
(d) M. Larhed, C. Moberg, A. Hallberg, Acc. Chem. Res. 35 (2002) 717;
(e) N. Kuhnert, Angew. Chem., Int. Ed. 41 (2002) 1863;
(f) P. Lindström, J. Tierney, B. Wathey, J. Westman, Tetrahedron 57 (2001) 9225–9283;
(g) C. Gabriel, S. Gabriel, E.H. Grant, B.S. Halstead, D.M.P. Mingos, Chem. Soc. Rev. 27 (1998) 213.
[13] (a) Y.T. Lee, S.Y. Choi, Y.K. Chung, Tetrahedron Lett. 48 (2007) 5673;
(b) Y.T. Lee, S.Y. Choi, S.I. Lee, Y.K. Chung, T.J. Kang, Tetrahedron Lett. 47 (2006) 6569.
[14] The yield of **2C** was rather independent of the activation time with a base. However, the situation was quite different for NHC ligands bearing no aryl group(s). For example, when **1J** was activated with a base for 2 h, the yield of **2J** was 25%. However, when **1J** was reacted with a base without an activation time, the yield of **2J** increased to 48%.
[15] (a) K. Öfele, W.A. Herrmann, D. Mihalios, M. Elison, E. Herdtweck, W. Scherer, J. Mink, J. Organomet. Chem. 459 (1993) 177,

Compound **2K** and its congeners were 53%, 47%, and 43%, respectively;

(b) H.G. Raubenheimer, Y. Stander, E.K. Marais, C. Thompson, G.J. Kruger, S. Cronje, M. Deetlefs, Organomet. Chem. 590 (1999) 158.

[16] Y. Yamaguchi, T. Kashiwabara, K. Ogata, Y. Miura, Y. Nakamura, K. Kobayashi, T. Ito, Chem. Commun. (2004) 2160.

[17] M.Y. Darensbourg, J.M. Hanckel, Organometallics 1 (1982) 82.