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Journal of Organometallic Chemistry 575 (1999) 141–144

Journal of Organometallic Chemistry

Synthesis of tricarbonyl(η^6-quinaldine)chromium(0) by a low pressure method

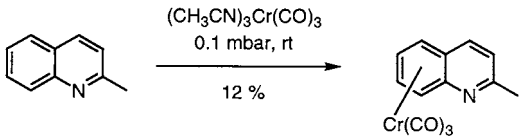
Regine Wolfgramm [a], Sabine Laschat [b,*]

[a] *Organisch-Chemisches Institut, Universität Münster, Corrensstr. 40, D-48149 Münster, Germany*
[b] *Institut für Organische Chemie, Technische Universität Braunschweig, Hagenring 30, D-38106 Braunschweig, Germany*

Received 18 August 1998;

Abstract

Several methods for the synthesis of tricarbonyl(η^6-quinaldine)chromium **4** were investigated. Whereas thermal and photochemical complexation gave exclusively pentacarbonyl(η^1-quinaldine)chromium **2**, thermal and high pressure ligand exchange reactions employing $(CH_3CN)_3Cr(CO)_3$ and tricarbonyl(η^6-naphthaline)chromium **3** respectively gave only low conversions. However, the desired complex **4** was obtained by a novel low pressure ligand exchange reaction in 12% yield.



Keywords: Chromium arene complex; Hetero arene complex; Quinoline; Ligand exchange reaction

1. Introduction

Since the discovery of η^6-chromium arene complexes in 1957 by Fischer and Öfele [1], they have widely been used in organic synthesis, because of the various steric and electronic effects of the chromium tricarbonyl moiety on the aromatic ring and the attached side chains [2–11]. The tendency of an aromatic ring to form π-bonds to a chromium fragment is generally decreased by anellation as compared to the parent benzene system. Consequently anellated aryl compounds usually gave only monochromiumtricarbonyl complexes with the chromium fragment being coordinated to the aryl ring with the largest index of local aromaticity, i.e. the terminal, least anellated ring [12–15]. Chromiumtricarbonyl complexes of electron-rich heteroaromatics, like thiophene and *N*-methylpyrrol show similar behavior compared to the carbocyclic arene complexes [16–20]. In contrast electron-poor heteroaromatics like pyridine favor the formation of η^1-complexes (σ-complexes), e.g. η^1-(py)$Cr(CO)_5$ or η^1-$(py)_3Cr(CO)_3$. However, η^1-complexation can be completely suppressed by the introduction of sterically bulky *ortho*-substituents which make the lone pair less easily accessible and thus the η^6-pyridine chromiumtricarbonyl complexes were formed [21–27]. In condensed heterocycles coordination of the chromium fragment to the terminal benzene ring is usually favored and the overall tendency to form π-complexes is controlled by the type of heterocycle [28]. Whereas indol-derived chromiumtricarbonyl complexes were easily accessible [29–31], the corresponding quinoline complexes were not known until now. We therefore aimed a program towards the synthesis of

* Corresponding author. Tel.: +49-531-3915264; fax: +49-531-3915388; e-mail: s.laschat@tu-bs.de.

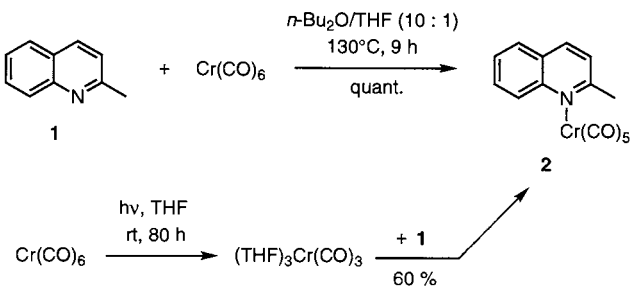
0022-328X/99/$ - see front matter
PII: S0022-328X(98)00987-5

π-complexes of quinoline derivatives. The results are described in this communication.

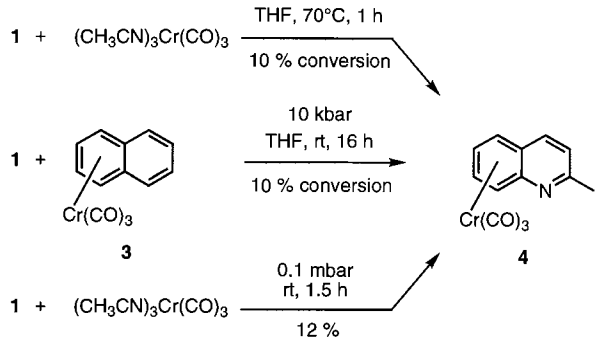
2. Results and discussion

In order to minimize σ-complexation quinaldine **1** was used instead of quinoline. Our initial attempts to synthesize the π-complex by standard methods were unsuccessful. Thus heating an equimolar mixture of quinaldine **1** and $Cr(CO)_6$ in di-*n*-butylether/THF (10:1) at reflux for several hours [32] resulted only in the formation of the σ-complex **2** (Scheme 1). Although the ^{1}H-NMR spectrum of **2** is similar to **1**, the presence of four CO stretching bands in the IR spectrum strongly supports σ-complexation. The spectral data are in good agreement with the known pentacarbonyl(η^1-pyridine)chromium(0) complex [33]. Following a photochemical route developed by Panell et al. [34] and Bickelhaupt [35] $(THF)_3Cr(CO)_3$ was generated by irradiation of $Cr(CO)_6$ in THF at 253 nm and then treated with quinaldine **1** to give only complex **2**.

Next we attempted the synthesis of the η^6-complex **4** via ligand exchange reactions. Treatment of quinaldine **1** with tricarbonyl(η^6-naphthaline)chromium(0) **3** at elevated temperatures [36] resulted only in decomposition of the naphthaline π-complex. However, heating **1** with $(CH_3CN)_3Cr(CO)_3$ in THF at 70°C [37] yielded 10% conversion towards the desired π-complex **4** (Scheme 2), as was indicated by the highfield shift of the ^{1}H-NMR signals of **4** as compared to the uncomplexed **1** (Fig. 1). Unfortunately the conversion could not be raised above 10% by prolonged reaction times. Variable temperature NMR spectra of the crude product (**1**:**4** = 90:10) between 233 and 353 K in toluene[D_8] showed, that the initial ratio of **1**:**4** remained constant between 233 and 323 K and decreased upon further heating to 343 K. At 353 K the signals of the π-complex **4** completely disappeared and no trace of the possible ligand exchange product tricarbonyl(η^6-[D_8]toluene) chromium was found. This thermal instability of **4** might be the reason why product **4** could not obtained by the above mentioned high temperature methods. In a different approach we tried ligand exchange reactions



Scheme 1.



Scheme 2.

under high pressure conditions [38]. In order to minimize thermal decomposition of **4** a mixture of quinaldine **1** and tricarbonyl(η^6-naphthaline)chromium(0) **3** in THF was pressurized at 10 kbar for 16 h. Monitoring the reaction by NMR showed again 10% conversion, which could not be increased by prolonged reaction times. Finally, a novel low pressure method was developed to overcome the problems described above. $(CH_3CN)_3Cr(CO)_3$ was dissolved in excess quinaldine **1** at room temperature and the ligand exchange reaction was promoted by stirring the mixture at 0.1 mbar thus evaporating the acetonitrile. After addition of *n*-heptane to the crude mixture pure complex **4** was isolated in 12% yield as a deep red crystalline solid. It should be mentioned that the low pressure method resulted in quantitative conversion in contrast to the other methods. Optimization of the crystallization procedure should improve the yield.

3. Conclusion

$(CH_3CN)_3Cr(CO)_3$ is sufficiently reactive to undergo a ligand exchange reaction with quinaldine **1** at room temperature under reduced pressure to yield the novel, thermolabile hetero-aromatic π-complex **4**.

4. Experimental

4.1. General

All reactions were carried out under an argon atmosphere using standard Schlenk techniques. Solvents were dried and deoxygenated by standard procedures. NMR spectra were recorded on a Bruker AC 200 P (200 MHz ^{1}H; 50 MHz ^{13}C), a Bruker ARX 300 (300 MHz ^{1}H; 75 MHz ^{13}C), and a Bruker AM 360 (360 MHz ^{1}H; 90 MHz ^{13}C) with a variable temperature unit. IR spectra: DIGILAB FTS-45 FT-IR spectrometer. Mass spectra: Finnigan MAT 312 spectrometer (ionization potential 70 eV). UV–vis spectra: Shimadzu

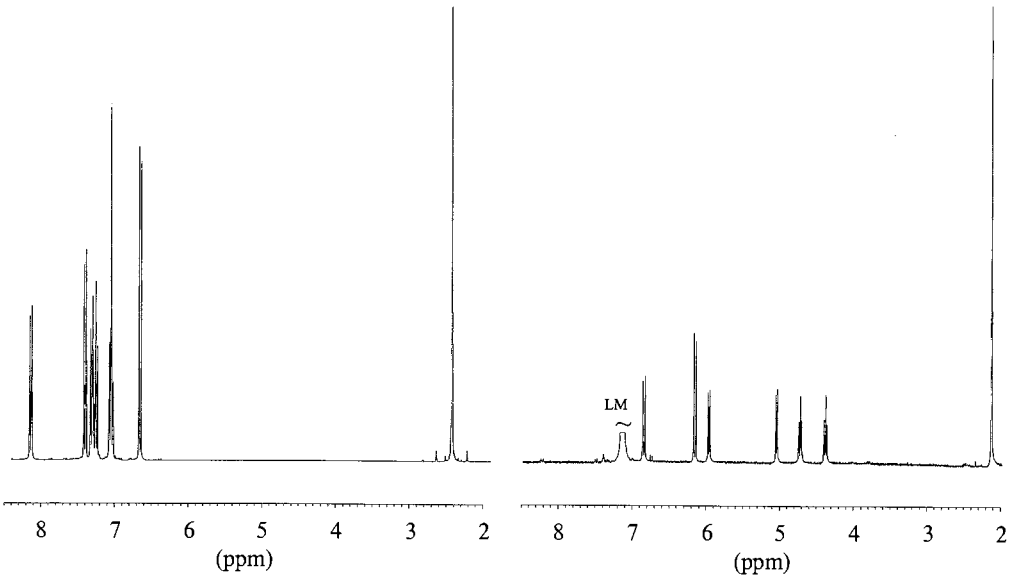


Fig. 1. ^{1}H-NMR spectra (300 MHz, C_6D_6) of quinaldine **1** (left) and tricarbonyl(η^6-quinaldine)chromium(0) **4** (right).

UV–vis recording spectrometer. The high pressure reactions were carried out in a Teflon ampoule with a high pressure apparatus (Andreas Hofer). The photochemical reactions were performed in a Rayonet photochemical chamber reactor Model RPR-100 (Southern New England Corporation) with RPR-2537 Å lamps. Tricarbonyl(η^6-naphthalene)chromium(0) **3** was prepared according to Ref. [39,40] and $(CH_3CN)_3Cr(CO)_3$ was prepared according to Ref. [41].

4.2. Thermal reaction of quinaldine *1* with $Cr(CO)_6$

To a solution of quinaldine **1** (715 mg, 5.00 mmol) in di-*n*-butylether/THF (25 ml, 10:1) was added $Cr(CO)_6$ (1.10 g, 5.00 mmol) and the mixture was heated for 9 h at 130°C. After cooling to room temperature the mixture was filtered via Celite and evaporated to give 1.68 g (quant.) of **2** as an orange solid, which was analyzed directly by IR and NMR.

4.3. Photochemical reaction of quinaldine *1* with $Cr(CO)_6$

A solution of $Cr(CO)_6$ (673 mg, 3.00 mmol) in THF (15 ml) was irradiated for 80 h at room temperature with a Hg lamp ($\lambda = 253$ nm). Then the orange solution was treated with quinaldine **1** (1.43 g, 10.0 mmol) and stirred for 24 h at room temperature. The solvent was evaporated in vacuo to give 603 mg (60%) of **2** as an orange solid.

4.4. Pentacarbonyl(η^1-quinaldine)chromium(0) *2*

M.p. 119°C; UV (CH_2Cl_2): λ_{max} (log ε) 264.5 (5.130), 278.0 (5.314), 302.0 (5.032), 315.5 (5.009), 380.5 (4.324); IR (KBr) 3046, 2070, 1980, 1933, 1899, 1621, 1601, 1561, 748, 657, 433 cm^{-1}; ^{1}H-NMR (200 MHz, C_6D_6) 8.25 (d, $J = 8.2$ Hz, 1H, 8-H), 7.52–7.32 (m, 3H, 4-H, 5-H, 7-H), 7.18–7.11 (m, 1 H, 6-H), 6.75 (d, $J = 8.3$ Hz, 1H, 3-H), 2.53 (s, 3H, CH_3); ^{13}C-NMR (50 MHz, C_6D_6) 211.5 (CO), 158.9 (C-2), 148.8 (C-8a), 135.6 (C-4), 129.7 (C-7), 129.3 (C-8), 127.6 (C-5), 126.8 (C-4a), 125.6 (C-6), 121.8 (C-3), 25.3 (CH_3).

4.5. Thermal reaction of quinaldine *1* with $(CH_3CN)_3Cr(CO)_3$

A solution of $(CH_3CN)_3Cr(CO)_3$ (1.30 g, 5.00 mmol) and quinaldine **1** (715 mg, 5.00 mmol) in THF (25 ml) was heated for 1 h at 70°C. Then the solvent was removed in vacuo to give 850 mg of a red oil, which contained 10% of **4** by ^{1}H-NMR. If the mixture was heated for 16 h instead, again 10% conversion were observed.

4.6. High pressure reaction of quinaldine *1* with tricarbonyl(η^6-naphthalene)-chromium(0) *3*

A solution of tricarbonyl(η^6-naphthalene)chromium(0) **3** (200 mg, 0.76 mmol) and quinaldine **1** (108 mg, 0.76 mmol) in THF (5 ml) was pressurized for 16

h at 10 kbar. Then the solvent was removed in vacuo to give 280 mg of red oil, which contained only 10% of **4** (by ^{1}H-NMR).

*4.7. Tricarbonyl(η^6-quinaldine)chromium(0) **4** via the low pressure method*

$(CH_3CN)_3Cr(CO)_3$ (259 mg, 1.00 mmol) was dissolved in quinaldine **1** (2.86 g, 20.0 mmol) and the resulting red mixture was stirred under vacuum (0.1 mbar) for 1.5 h at room temperature. After flushing the mixture with argon, *n*-heptane (30 ml) was added and the mixture was stirred for 12 h at room temperature. The deep red heptane layer was separated and stored for 12 h in the freezer. The precipitate was filtered via a fritted funnel and dried in vacuo to give 31 mg (12%) of red crystals. M.p. 136°C; UV (CH_2Cl_2): λ_{max} (log ε) 239.0 (4.588), 316.5 (4.291), 338.5 (4.283), 458.0 (3.859); IR (KBr) 2959, 2920, 1973, 1898, 1845, 1613, 1464, 1376, 664, 617; ^{1}H-NMR (300 MHz, C_6D_6) 6.87 (d, $J = 8.7$ Hz, 1H, 4-H), 6.18 (d, $J = 8.7$ Hz, 1H, 3-H), 5.98 (d, $J = 6.7$ Hz, 1H, 8-H), 5.06 (d, $J = 6.4$ Hz, 1H, 5-H), 4.74 (dd, $J = 6.7/6.1$ Hz, 1H, 7-H), 4.40 (d, $J = 6.4/6.1$ Hz, 1H, 6-H), 2.15 (s, 3H, CH_3); ^{13}C-NMR (50 MHz, C_6D_6) 232.0 (CO), 165.2 (C-2), 149.5 (C-8a), 138.2 (C-4), 123.0 (C-3), 121.5 (C-4a), 94.4 (C-5), 91.0, 90.5, 89.7 (C-6, C-7, C-8), 25.3 (CH_3); MS(EI) *m*/*z* 279 (M, 24), 223 (M-2 CO, 20), 221 (8), 195 (M-3 CO, 55), 149 (61), 143 [M–$Cr(CO)_3$, 80], 128 (M–$Cr(CO)_3$–CH_3, 54), 115 (73), 91 (52), 83 (58), 77 (71), 75 (72), 57 (75), 52 (Cr, 100).

Acknowledgements

Generous financial support by the Deutsche Forschungsgemeinschaft (Gerhard-Hess-Preis for S.L.), the Alfried Krupp von Bohlen und Halbach-Stiftung and the Fonds der Chemischen Industrie is gratefully acknowledged. We would like to thank D. Wingbermühle for technical assistance with photochemical and high pressure reactions.

References

[1] E.O. Fischer, K. Öfele, Chem. Ber. 90 (1957) 2532.
[2] S.G. Davies, T.J. Donohoe, Synlett (1993) 323, review.
[3] M. Semmelhack, in: B.M. Trost (Ed.), Comprehensive Organic Synthesis, vol. 4, Pergamon Press, London, 1994, p. 517, review.
[4] S.G. Davies, S.J. Coote, C.L. Goodfellow, in: L.S. Liebeskind (Ed.), Advances in Metal-Organic Chemistry, vol. 2, JAI Press, Greenwich, CT, 1991, p. 1, review.
[5] A. Solladie-Cavallo, in: L.S. Liebeskind (Ed.), Advances in Metal-Organic Chemistry, vol. 1, JAI Press, Greenwich, CT, 1991, p. 99, review.
[6] M. Uemura, in: L.S. Liebeskind (Ed.), Advances in Metal-Organic Chemistry, vol. 2, JAI Press, Greenwich, CT, 1991, p. 195, review.
[7] H.G. Schmalz, S. Siegel, J.W. Bats, Angew. Chem., Int. Ed. Engl. 34 (1995) 2383.
[8] E.P. Kündig, L. He Xu, P. Romanens, G. Bernardinelli, Synlett (1996) 270.
[9] G.B. Jones, S.B. Heaton, Tetrahedron Asymmetry 4 (1993) 261.
[10] M. Sodeoka, M. Shibasaki, Synlett (1993) 643.
[11] Y. Hayashi, H. Sakai, N. Kasseta, M. Uemura, J. Organomet. Chem. 503 (1995) 143.
[12] B. Deubzer, H.P. Fritz, C.G. Kreiter, K. Öfele, J. Organomet. Chem. 7 (1967) 289.
[13] B. Deubzer, E.O. Fischer, H.P. Fritz, C.G. Kreiter, N. Kriebitzsch, H.D. Simmons, B.R. Willeford, Chem. Ber. 100 (1967) 3084.
[14] E.O. Fischer, K. Öfele, Z. Naturforsch. 13b (1958) 458.
[15] R.B. King, F.G.A. Stone, J. Am. Chem. Soc. 82 (1960) 4557.
[16] M.F. Bailey, L.F. Dahl, Inorg. Chem. 4 (1965) 1306.
[17] K. Öfele, Chem. Ber. 99 (1966) 1732.
[18] K. Öfele, E. Dotzauer, J. Organomet. Chem. 30 (1971) 211.
[19] M.S. Loft, T.J. Mowlem, D.A. Widdowson, J. Chem. Soc. Perkin Trans. 1 (1995) 97.
[20] M.S. Loft, T.J. Mowlem, D.A. Widdowson, D.J. Williams, J. Chem. Soc. Perkin Trans. 1 (1995) 105.
[21] P.L. Timms, Angew. Chem. Int. Ed. Engl. 14 (1975) 273.
[22] H.-G. Biedermann, K. Öfele, N. Schuhbauer, J. Tajtelbaum, Angew. Chem, Int. Ed. Eng. 14 (1975) 639.
[23] K. Dimroth, R. Thamm, H. Kaletch, Z. Naturforsch. 39b (1984) 207.
[24] H.W. Choi, M.S. Sollberger, J. Organomet. Chem. 243 (1983) 39.
[25] S.G. Davies, M.R. Shipton, J. Chem. Soc. Perkin Trans. 1 (1991) 501.
[26] S.G. Davies, M.R. Shipton, J. Chem. Soc. Perkin Trans. 1 (1991) 757.
[27] S.G. Davies, A.J. Edwards, M.R. Shipton, J. Chem. Soc. Perkin Trans. 1 (1991) 1009.
[28] E.O. Fischer, H.A. Goodwin, C.G. Kreiter, H.D. Simmons, K. Sonogashira, S.B. Wild, J. Organomet. Chem. 14 (1968) 359.
[29] M.F. Semmelhack, W. Wulff, J.L. Garcia, J. Organomet. Chem. 240 (1982) 5.
[30] M.F. Semmelhack, G.R. Clark, J.L. Garcia, J.J. Harrison, Y. Thatanonth, W. Wulff, A. Yamashita, Tetrahedron 37 (1981) 3957.
[31] E. Furet, F. Savary, J. Weber, E.P. Kündig, Helv. Chim. Acta 77 (1994) 2117.
[32] C.A.L. Mahaffy, P.L. Pauson, Inorg. Synth. 19 (1979) 154.
[33] C.S. Kraihanzel, F.A. Cotton, Inorg. Chem. 2 (1963) 533.
[34] K.H. Panell, D.C. Hambrick, G.S. Lewandos, J. Organomet. Chem. 99 (1975) 21.
[35] G.B.M. Klostermans, M. Bobeldijk, P.J. Kwakman, W.H. de Wolf, F. Bickelhaupt, J. Organomet. Chem. 363 (1989) 291.
[36] E.P. Kündig, C. Perret, S. Spichiger, G. Bernardinelli, J. Organomet. Chem. 286 (1985) 183.
[37] D.P. Tate, W.R. Knipple, J.M. Angl, Inorg. Chem. 1 (1962) 433.
[38] G. Natta, R. Erzoli, F. Calderazzo, Chim. Ind. 40 (1958) 287.
[39] E.O. Fischer, K. Öfele, H. Essler, W. Fröhlich, J.P. Martensen, W. Semmlinger, Chem. Ber. 91 (1958) 2763.
[40] B. Nicholls, M.C. Whiting, J. Chem. Soc. (1959), 551.
[41] D.P. Tate, W.R. Knipple, J.M. Augl, Inorg. Chem. 1 (1962) 433.