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The formation and reactions of some new functionally substituted derivatives of (η^5-cyclopentadienyl) dicarbonylnitrosylchromium (cynichrodene) †

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Abstract

A reaction between cynichrodenoic acid, (η^5-C_5H_4COOH)$Cr(CO)_2NO$ (**6**) and phosphorus pentachloride produces cynichrodenoyl chloride (**11**) in high yield. Subsequent reaction of **11** with sodium azide affords cynichrodenoyl azide (**12**), which undergoes Curtius rearrangement to form cynichrodenyl isocyanate (**13**). Subsequent hydrolysis of isocyanate **13** in aqueous KOH solution yields aminocynichrodene (**14**). Azide **12** also undergoes Curtius rearrangement in the presence of benzyl alcohol to produce benzyl *N*-cynichrodenylcarbamate (**15**). Reactions of acid chloride **11** with ammonia, dimethylamine or aniline lead to the corresponding carboxamides (**16–18**). Amide **16** is readily dehydrated to produce cynichrodenecarbonitrile (**19**). Reactions of acid chloride **11** with either benzyl alcohol or hydroxymethylferrocene generate the corresponding esters (**20–21**), whereas treatment of a tetrahydrofuran solution of **11** with pyridine affords cynichrodenecarboxylic anhydride (**22**) in low yield. Reactions of acetylcynichrodene (**2**) with organolithium reagents, leading to both carbonyl addition and condensation products, have been investigated. Treatment of **2** with lithium diisopropylamide in diethyl ether solution produces the self-condensation product 1,3-dicynichrodenyl-but-2-en-1-one (**24**). Acetyl derivative **2** and benzaldehyde also undergo Claisen–Schmidt condensation in the presence of lithium diisopropylamide to afford cinnamoylcynichrodene (**27**).

Introduction

Functionally substituted derivatives of (η^5-cyclopentadienyl)dicarbonylnitrosylchromium (**1**) (hereafter called cynichrodene [1*]) have been the subject of continuing interest in our laboratory. The Friedel–Crafts acetylation of **1** to form acetylcynichrodene (**2**) was first described by Fischer and Plesske [2] in 1961. We

† Dedicated to Professor P.L. Pauson on the occasion of his 65th birthday.
* Reference number with asterisk indicates a note in the list of references.

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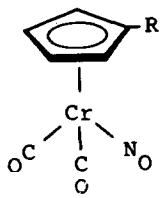


1	R = H	**8**	R = COOMe	**15**	R = $NHCOOCH_2Ph$
2	R = C(O)Me	**9**	R = C≡CH	**16**	R = $C(O)NH_2$
3	R = $CH{=}CH_2$	**10**	R = C(O)SPh	**17**	R = $C(O)NMe_2$
4	R = C(O)Ph	**11**	R = C(O)Cl	**18**	R = C(O)NHPh
5	R = C(O)SMe	**12**	R = $C(O)N_3$	**19**	R = C≡N
6	R = COOH	**13**	R = NCO	**20**	R = COOBz
7	R = CHO	**14**	R = NH_2	**21**	R = $COOCH_2Fc$

subsequently demonstrated that sodium borohydride reduction of **2** followed by acid-catalyzed dehydration produced vinylcynichrodene (**3**) in good overall yield [3].

Compound **3** underwent homo- and copolymerizations in the presence of azo initiators, and was found to be an exceptionally electron-rich vinyl monomer, resembling vinylferrocene and and vinylcymantrene [3,4]. Further studies on the acylation of **1** afforded benzoyl (**4**) and (methylthio)carbonyl (**5**) derivatives. Ketones **2** and **4** underwent a variety of reduction and addition reactions, whereas **5** could be hydrolyzed under basic conditions to produce cynichrodenoic acid (**6**) [5]. In an alternative synthetic approach, reactions of formyl-, acetyl-, or carbomethoxycyclopentadienylsodium with $Cr(CO)_6$ in dimethylformamide at reflux, followed by treatment of the resulting anions with acetic acid and subsequent nitrosylation, produced the respective derivatives **7**, **2** and **8** in excellent yield [6]. Additional studies on the reactivities of these products were undertaken, including the hydrolysis of **8** to form **6**, and the conversion of **2** into ethynylcynichrodene (**9**) [6].

A detailed study of ^1H and ^{13}C NMR spectra of a series of cynichrodene-stabilized carbonium ions has been undertaken. The data indicate that these cations are stabilized in a manner similar to isoelectronic ferrocenyl and cymantrenyl carbonium ions [7]. pK_{R^+} values of cynichrodene-stabilized carbonium ions have been measured [8]. A dimetallocenyl-stabilized carbonium ion, α-cynichrodenyl-α-ferrocenylmethylium tetrafluoroborate, has also recently been synthesized and characterized [9].

In an effort to further expand the area of functionally substituted derivatives of **1**, we report here on the conversion of carboxylic acid **6** into a series of derivatives, and on an examination of their reactivity. Also described are several base-induced condensation reactions of the acetyl derivative **2**.

Results and discussion

Derivatives of cynichrodenoic acid (6)

Previous studies have shown that a Friedel–Crafts type reaction between **1**, methylchlorothioformate and aluminum chloride produced **5** in 71% yield. Subsequent hydrolysis of **5** under basic conditions gave **6** in 50% yield [5]. Since acid **6** could serve as an important starting material in the further development of

cynichrodene chemistry, it was of initial interest to determine if modifications of this procedure could lead to improved yields of **6**.

A Friedel–Crafts type reaction in which **1** in methylene chloride solution was added to a previously prepared and filtered solution of aluminum chloride and phenylchlorothioformate produced, after hydrolysis, column chromatography and vacuum distillation, and 88% yield of (phenylthio)carbonylcynichrodene (**10**). Basic hydrolysis of the thio-ester **10** with potassium hydroxide in n-propyl alcohol under conditions previously described [5] gave the desired acid **6** in ca. 70% yield. This route to **6** is thus a distinct improvement over the original route, both in terms of product yield as well as the convenience and availabilities of the acylating agents. Earlier pK_a studies have demonstrated that **6** is a weaker acid than are either ferrocenoic acid or benzoic acid, and is approximately as strong an acid as *m*-(methylamino)benzoic acid [5].

In a manner analogous to the formation of ferrocenoyl chloride, chlorocarbonylcynichrodene (cynichrodenoyl chloride) (**11**) has been prepared in 94% yield from a reaction between **6** and phosphorus pentachloride in dry benzene at room temperature [10]. Compound **11** could be obtained analytically pure by vacuum sublimation at 50 °C. However, in most studies **11** was not isolated in pure form, but prepared from **1** in each experiment and used as a reaction intermediate. The yields of the new products described below are therefore based on **6** as the starting material, not **11**.

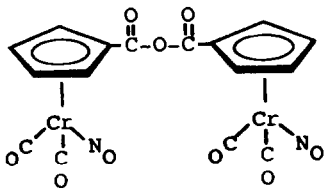
Acid chloride **11** reacted readily with sodium azide in aqueous tetrahydrofuran solution to afford cynichrodenyl azide (**12**) in 62% yield. The azide **12** underwent a Curtius rearrangement when refluxed in benzene solution, and cynichrodenyl isocyanate (**13**) could be obtained in 72% yield. Subsequent hydrolysis of isocyanate **13** by means of 20% aqueous potassium hydroxide under reflux conditions resulted in the formation of aminocynichrodene (**14**) in 75% yield. Amine **14** has been previously isolated in very low yield from a reaction between lithium nitrocyclopentadienide and $Cr(CO)_6$, followed by acidification and nitrosylation [6]. This latter unexpected result represented the first example of the reduction of a nitrocyclopentadienide ion.

Azide **12** also underwent Curtius rearrangement in the presence of benzyl alcohol to form the urethane derivative benzyl *N*-cynichrodenylcarbamate (**15**) in 73% yield. Treatment of **15** with a hydrobromic acid/acetic acid mixture likewise produced a 50% yield of amine **14** based on **15**.

Reactions of acid chloride **11** with ammonia, amines and aniline led to the corresponding carboxamide derivatives of **1**. Thus, when **11** in diethyl ether solution was treated with ammonia or with dimethylamine, cynichrodenecarboxamide (**16**) and *N,N'*-dimethylcynichrodenecarboxamide (**17**) were obtained in yields of 76% and 82%, respectively. A similar reaction between **11** and aniline resulted in a 76% yield of *N*-phenylcynichrodenecarboxamide (**18**). When the amide **16** was refluxed in acetic anhydride for 1 h, it was readily dehydrated to produce cynichrodenecarbonitrile (**19**) in 75% yield.

Reactions of acid chloride **11** to form oxygenated derivatives were also investigated. Thus, a reaction of **11** with benzyl alcohol gave benzyl cynichrodenate (**20**) in 82% yield, whereas treatment of **11** with hydroxymethylferrocene led to ferrocenylmethyl cynichrodenate (**21**) in 46% yield. Furthermore, the acid anhydride derivative cynichrodenecarboxylic anhydride (**22**) could be obtained in 30% yield by

heating a tetrahydrofuran solution of the acid chloride **11** containing the acid **6** in the presence of pyridine for 5 min.



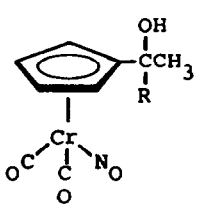
22

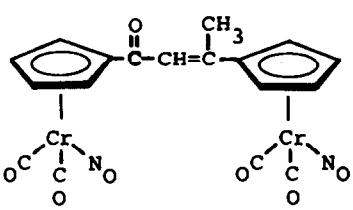
Condensation reactions of acetylcynichrodene (2)

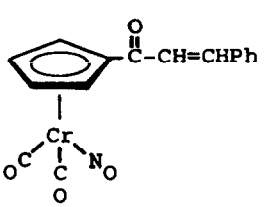
We have previously reported that the ketones **2** and **4** react with alkyl- or arylmagnesium halides to form the corresponding tertiary alcohols in high yields. Subsequent studies on reactions of the acetyl derivative **2** with several organolithium reagents have led to somewhat surprising results. Thus, a reaction between equimolar amounts of **2** and phenyllithium in diethyl ether afforded the normal carbonyl addition product 1-cynichrodenyl-1-phenylethanol (**23**) in 60% yield, as well as the condensation product 1,3-dicynichrodenyl-but-2-en-1-one (**24**) in 13% yield. The two products could be conveniently separated by column chromatography on alumina.

Compound **24** was obtained as a red liquid and was characterized by IR, ^{1}H NMR and mass spectrometry. The ^{1}H NMR spectrum exhibited a 3-proton doublet at δ 2.35 ppm for the CH_3 protons, a 4-proton multiplet at δ 5.18 ppm for the H(3, 4) protons on the two substituted cyclopentadienyl rings, a 2-proton triplet at δ 5.52 ppm for the H(2, 5) protons of the cyclopentadienyl ring substituted by the alkenyl carbon, a 2-proton triplet at δ 5.78 ppm for the H(2, 5) protons on the cyclopentadienyl ring substituted by the carbonyl carbon, and a 1-proton quartet at δ 6.50 ppm for the proton on the alkenyl carbon atom. Compound **24** also gave a suitable C, H and N analysis, and a molecular weight of 472 was confirmed by virtue of a strong molecular ion at this value in the mass spectrum of **24**.

A similar result occurred from a reaction between **2** and n-butyllithium, although in this instance the corresponding carbonyl addition product (**25**) and the con-







23 R = Ph

25 R = n-Bu

26 R = Me

24

27

densation product **24** could not be separated by column chromatography. ^{1}H NMR analysis indicated that the two products were each obtained in ca. 33% yield, however. In contrast, only the carbonyl addition product 1-hydroxy-1-methyl-ethyl-cynichrodene (**26**) was isolated (93%) when equimolar amounts of **2** and methyl-lithium were allowed to react under similar conditions.

It is obvious that **24** is formed by a base-promoted condensation of two molecules of ketone **2** followed by the elimination of H_2O. Aldol-type condensation reactions of methyl metallocenyl ketones of this type are well-known to occur under basic conditions. Thus, self-condensations of both acetylferrocene and acetylcymantrene to form the corresponding 1,3-disubstituted but-2-en-1-one derivatives have been previously reported in the literature, employing potassium tert-butoxide in refluxing benzene [11] and sodium amide in diethyl ether [12], respectively. In the present reactions, phenyl- or n-butyllithium evidentally functions in part to abstract a hydrogen from the α-carbon atom of **2**, generating a carbanion which subsequently adds to the carbonyl group of another molecule of **2**.

Earlier, studies have shown that bases such as sodium ethoxide and potassium tert-butoxide are capable of promoting base-condensation reactions of acetylferrocene and acetylcymantrene. In the present study, however, all attempts to employ these bases in condensations of **2** failed, and starting ketone could be largely recovered. It would thus appear that the methyl hydrogens of **2** are less acidic relative to other metallocenyl analogs.

A non-organometallic base, lithium diisopropylamide (LDA), was subsequently found to be useful in promoting base condensation reactions of **2**. This reagent, which is basic yet non-nucleophilic towards carbonyl groups, effected the self-condensation of **2** to form **24** in 54% yield. The reaction is therefore much superior for promoting the self-condensation reaction of **2**, since undesired products resulting from carbonyl addition or degradation of the cynichrodenyl moiety can be avoided.

In view of the success in using LDA for promoting the self-condensation of **2**, we attempted a Claisen–Schmidt reaction under these conditions. Thus, an equimolar mixture of **2** and benzaldehyde were added to LDA in diethyl ether, and the reaction mixture was allowed to stir for 3 h. Following hydrolysis and column chromatography, an 89% yield of the mixed condensation product cinnamoyl-cynichrodene (**27**) was obtained.

Spectral studies

We have previously discussed the ^{1}H NMR, IR and mass spectra of a variety of monosubstituted cynichrodenes in considerable detail [5]. Similar conclusions apply to all the new cynichrodene compounds reported herein. Spectral features of each compound are given in the Experimental section.

Conclusions

The above results demonstrate that cynichrodenoic acid (**6**) behaves in large measure as a typical aromatic carboxylic acid, as does ferrocenoic acid. The carbonyl and nitrosyl substituents which are coordinated to the chromium atom do not interfere to any significant extent in the conversion of **6** into its acid chloride derivative **11**, or in subsequent transformations of **11** into amide, ester, anhydride, nitrile or Curtius rearrangement products.

Condensation reactions involving acetylcynichrodene **2** can occur under a variety of basic conditions. For any future studies of this type, however, it would seem that LDA would be the reagent of choice to promote such reactions.

Experimental

All operations were carried out under either an argon or a nitrogen atmosphere by means of Schlenk techniques. The argon or nitrogen was dried with H_2SO_4 and P_2O_5, and trace oxygen was removed by activated BTS catalyst. Hexane, pentane, benzene, methylene chloride and dimethylformamide were dried over calcium hydride and freshly distilled under argon from calcium hydride. Diethyl ether was predried over sodium and distilled under argon from sodium-benzophenone ketyl radical. Tetrahydrofuran (THF) was predried with potassium hydroxide, then with sodium and finally distilled under argon from sodium-benzophenone ketyl radical. All other solvents were used as obtained commercially. Column chromatography was carried out under argon or nitrogen using Fisher silica gel, CAMAG neutral alumina, or Florisil. The adsorbents were heated with a heat gun while mixing on a rotary evaporator attached to a vacuum pump for 2 h to remove water and oxygen. In the case of the alumina, it was then deactivated with 5% (by weight) argon-saturated water. The adsorbents were stored under argon until use. ^{1}H NMR spectra were recorded on either Varian A-60 or Perkin Elmer R-12A spectrometers. IR spectra were obtained on either Perkin Elmer 237B or Beckman IR-10 spectrometers using KBr pellets or solutions, and were calibrated versus polystyrene. Mass spectra were obtained using a Perkin Elmer–Hitachi RMU 6L mass spectrometer. Melting points were determined on a Mel-Temp apparatus in sealed tubes under nitrogen or argon and are uncorrected. Microanalyses were performed by the Microanalytical Laboratory, University of Massachusetts, Amherst, MA.

*[(Phenylthio)carbonyl]cynichrodene (**10**)*

To a solution of cynichrodene (5.00 g, 24.6 mmol) in 50 ml of methylene chloride was slowly added a previously prepared and filtered solution of aluminum chloride (6.50 g, 48.7 mmol) and phenylchlorothioformate (6.39 g, 37 mmol) in 100 ml of methylene chloride. After the addition was completed, the reaction mixture was stirred at room temperature for 12 h. The reaction mixture was then cooled to 0 °C and slowly hydrolyzed with 200 ml of ice water followed by 10 drops of concentrated hydrochloric acid. The aqueous and organic layers were separated. The organic layer was washed with water several times, once with sodium bicarbonate solution, once again with water and dried with anhydrous magnesium sulfate. The solution was filtered, concentrated and chromatographed on a dry-packed column (4 × 9 cm) of silica gel. Elution of the column with hexane and removal of the solvent under vacuum gave 7.34 g (88%) of [(phenylthio)carbonyl]cynichrodene. An analytical sample was obtained by vacuum distillation at 145 °C/0.1 Torr. (Found: C, 49.79; H, 2.83; N, 3.84. $C_{14}H_9CrNO_4S$ calc.: C, 49.56; H, 2.67; N, 4.13%). ^{1}H NMR ($CDCl_3$) δ 5.14 (2H, t, $H_{3,4}$); 5.85 (2H, t, $H_{2,5}$); 7.44 (5H, s, C_6H_5). IR (CH_2Cl_2) 3080 (w), 2940 (w), 1965 (vs), 1700 (vs), 1680 (vs), 1640 (m), 1580 (w), 1480 (m), 1450 (m), 1400 (m), 1372 (m), 1240 (m), 1050 (s), 1036 (s), 1020 (m), 945 (s), 820 (vs), 660 (w) cm^{-1}. MS *m/e* 339 (M^+).

Cynichrodenoyl chloride (11)

Cynichrodenoic acid (1.00 g, 4.05 mmol) was stirred with phosphorus pentachloride (0.930 g, 4.47 mmol) in 50 ml of dry benzene for 2 h at room temperature. The reaction mixture was filtered and the filtrate concentrated in vacuum at 50 °C to remove the benzene and phosphorus oxychloride, leaving 1.01 g (94%) of cynichrodenoyl chloride as a red-brown residue. An analytical sample, m.p. 42.5 °C, was obtained by vacuum sublimation at 50 °C/0.1 Torr. (Found: C, 36.29; H, 1.62; N, 5.15. $C_8H_4ClCrNO_4$ calc.: C, 36.18; H, 1.53; N, 5.27%). ^{1}H NMR ($CDCl_3$) δ 5.25 (2H, t, $H_{3,4}$); 5.92 (2H, t, $H_{2,5}$). IR ($CDCl_3$) 3120 (w), 2036 (vs), 1980 (vs), 1765 (s), 1720 (vs), 1550 (w), 1446 (m), 1370 (m), 1256 (s), 1050 (m), 938 (m), 830 (m), 790 (s), 620 (m) cm^{-1}. MS *m/e* 265 (M^+).

Cynichrodenoyl azide (12)

Cynichrodenoic acid (1.00 g, 4.05 mmol) was stirred with phosphorus pentachloride (0.93 g, 4.47 mmol) in 50 ml of dry benzene for 2 h at room temperature. The reaction mixture was filtered and the filtrate concentrated in vacuum at 50 °C to remove the benzene and phosphorus oxychloride, giving a red-brown residue of cynichrodenoyl chloride. The residue was dissolved in 15 ml of THF and treated all at once with sodium azide (0.400 g, 6.15 mmol) in several ml of water. After 30 min at room temperature, 25 ml of ice water was poured into the reaction mixture and it was stirred for 15 min. The reaction mixture was then extracted with three 25-ml portions of ether. The extracts were combined, dried over magnesium sulfate, and concentrated to a dark brown residue. The residue was extracted with hot hexane/pentane (2 : 1), concentrated and chromatographed on a dry-packed column (4 × 9 cm) of silica gel. Elution of the column with 1 : 1 hexane/benzene gave an orange band which upon removal of the solvent under vacuum gave cynichrodenoyl azide, 0.69 g (62%). An analytical sample was obtained by molecular distillation at 65 °C/0.1 Torr. (Found: C, 35.55; H, 1.64; N, 20.43. $C_8H_4CrN_4O_4$ calc.: C, 35.31; H, 1.48; N, 20.58%). ^{1}H NMR ($CDCl_3$) δ 5.15 (2H, t, $H_{3,4}$); 5.80 (2H, t, $H_{2,5}$). IR (CH_2Cl_2) 2180 (m), 2164 (vs), 2036 (vs), 1970 (vs), 1710 (vs), 1470 (s), 1380 (s), 1260 (s), 1185 (vs), 1120 (w), 1060 (s), 1044 (m), 998 (s), 898 (w), 832 (s), 670 (s) cm^{-1}. MS *m/e* 272 (M^+).

Cynichrodenyl isocyanate (13)

Cynichrodenoyl azide was prepared as a dark brown solid from 1.00 g of cynichrodenoic acid as described above. Without further purification, the dark brown solid was dissolved in 50 ml of benzene and refluxed for 3 h. The benzene solution was filtered and then evaporated in vacuum to yield cynichrodenyl isocyanate as a brown oil, 0.71 g (72%). An analytical sample was obtained by molecular distillation at 60 °C/0.1 Torr. (Found: C, 39.40; H, 1.67; N, 11.61. $C_8H_4CrN_2O_4$ calc.: C, 39.36; H, 1.65; N, 11.48%). ^{1}H NMR ($CDCl_3$) δ 4.84 (2H, t, $H_{3,4}$); 5.06 (2H, t, $H_{2,5}$). IR ($CDCl_3$) 2220 (vs), 2030 (vs), 1960 (vs), 1710 (vs), 1550 (m), 1490 (w), 1400 (w), 870 (s) cm^{-1}. MS *m/e* 244 (M^+).

Benzyl N-*cynichrodenylcarbamate (15)*

Cynichrodenoyl azide was prepared as a dark brown solid from 1.00 g of cynichrodenoic acid as described above. Without further purification, 5 ml of benzyl alcohol was added and the mixture was heated for 3 h in an oil bath at 100–140 °C.

After removal of the solvent in vacuum, the residue was extracted with 100 ml of hot benzene/methylene chloride (1 : 1). Following filtration and evaporation of the solvent, the residue was chromatographed on a dry-packed column (4 × 9 cm) of silica gel. Elution of the column with benzene gave an orange band which upon removal of the solvent under vacuum gave benzyl *N*-cynichrodenylcarbamate, 1.04 g (73%). An analytical sample was obtained by molecular distillation at 140 °C/0.1 Torr. (Found: C, 51.14; H, 3.56; N, 7.76. $C_{15}H_{12}CrN_2O_5$ calc.: C, 51.14; H, 3.43; N, 7.95%). ^{1}H NMR ($CDCl_3$) δ 4.85 (2H, t, $H_{3,4}$); 5.21 (4H, m, CH_2 and $H_{2,5}$); 6.48 (1H, bs, NH); 7.38 (5H, s, C_6H_5). IR ($CDCl_3$) 3400 (s), 2020 (vs), 1950 (vs), 1735 (s), 1700 (vs), 1535 (s), 1400 (m), 1352 (m), 1232 (s), 1195 (s), 1072 (m), 1065 (m), 1035 (m), 1022 (m), 815 (m), 620 (m) cm^{-1}. MS *m/e* 324 $(M - CO)^+$.

Aminocynichrodene (14)

Cynichrodenyl isocyanate was prepared as a brown oil from 1.00 g of cynichrodenoic acid as described above. Ten milliliters of 20% aqueous potassium hydroxide solution was added and the mixture refluxed for 1.5 h, cooled, and extracted with three 25-ml portions of ether and one 25 ml portion of THF. The extracts were combined, dried over magnesium sulfate, and concentrated to a brown residue which was chromatographed on a dry-packed column (4 × 9 cm) of silica gel. Elution of the column with benzene gave a yellow-orange band which upon removal of the solvent under vacuum gave aminocynichrodene, 0.66 g (75%). An analytical sample, m.p. 61 °C, was obtained by vacuum sublimation at 65 °C/0.1 Torr. (Found: C, 38.67; H, 2.98; N, 12.70. $C_7H_6CrN_2O_3$ calc.: C, 38.54; H, 2.77; N, 12.84%). ^{1}H NMR ($CDCl_3$) δ 3.25 (2H, bs, NH_2); 4.60 (2H, t, $H_{3,4}$); 4.81 (2H, t, $H_{2,5}$). IR ($CDCl_3$) 3420 (m), 2020 (vs), 1950 (vs), 1690 (vs), 1622 (m), 1520 (s), 1402 (w), 1028 (w), 818 (m), 675 (w), 630 (s) cm^{-1}. MS *m/e* 218 (M^+).

Cynichrodenecarboxamide (11)

Cynichrodenoyl chloride was prepared as a red-brown solid from 1.00 g of cynichrodenoic acid as described above. Diethyl ether (20 ml) was added and dry ammonia passed through the solution for 30 min. There was an immediate precipitation of yellow crystals. After removal of the solvent, the residue was taken up in 50 ml of methylene chloride and the solution washed with water, dilute hydrochloric acid, and then again with water. After drying over magnesium sulfate, the solution was concentrated to a dark brown residue which was chromatographed on a dry-packed column (4 × 9 cm) of silica gel. Elution of the column with ether/THF gave an orange band which upon removal of the solvent under vacuum gave cynichrodenecarboxamide, 0.76 g (76%). An analytical sample was obtained by vacuum sublimation at 120 °C/0.1 Torr, mp 141.5 °C. (Found: C, 39.04; H, 2.71; N, 11.19. $C_8H_6CrN_2O_4$ calc.: C, 39.04; H, 2.46; N, 11.38%). ^{1}H NMR ($CDCl_3$) δ 2.82 (2H, s, NH_2); 5.33 (2H, t, $H_{3,4}$); 5.94 (2H, t, $H_{2,5}$). IR ($CDCl_3$) 3530 (w), 3420 (m), 2036 (vs), 1965 (vs), 1710 (vs), 1592 (m), 1480 (w), 1390 (w), 1360 (w), 1340 (w), 830 (m), 640 (m), 630 (m) cm^{-1}. MS *m/e* 246 (M^+).

Cynichrodenecarbonitrile (19)

Cynichrodenoyl chloride was prepared as a red-brown residue from 1.00 g of cynichrodenoic acid as described above. Diethyl ether (20 ml) was added and dry ammonia was passed through the solution for 30 min, resulting in the formation of

yellow crystals. After removal of the solvent, the residue was taken up in 50 ml of methylene chloride and the solution washed with water, dilute hydrochloric acid, and again with water. After drying over magnesium sulfate, the solution was concentrated to a dark brown residue. Without further purification, 20 ml of acetic anhydride was added and the reaction mixture was refluxed for 1 h. The reaction mixture was slowly added to 20 ml of water, and the aqueous solution was extracted with three 100-ml portions of ether. The combined organic extracts were washed once with water, once with sodium bicarbonate solution, once again with water, and were dried with magnesium sulfate. The solution was filtered and concentrated to a brown residue which was chromatographed on a dry-packed column (4 × 9 cm) of silica gel. Elution of the column with benzene gave a yellow band which upon removal of the solvent under vacuum gave cynichrodenecarbonitrile, 0.70 g (75%). An analytical sample, m.p. 50 °C, was obtained by vacuum sublimation at 45 °C/0.1 Torr. (Found: C, 42.27; H, 2.01; N, 12.26. $C_8H_4CrN_2O_3$ calc.: C, 42.12; H, 1.77; N, 12.28%). ^{1}H NMR ($CDCl_3$) δ 5.15 (2H, t, $H_{3,4}$); 5.60 (2H, t, $H_{2,5}$). IR ($CDCl_3$) 3150 (w), 2950 (w), 2270 (s), 2035 (vs), 1960 (vs), 1710 (vs), 1655 (w), 1615 (w), 1540 (w), 1410 (w), 1110 (w), 1040 (w), 1018 (w), 960 (w), 810 (m) cm^{-1}. MS *m/e* 228 (M^+).

N-*Phenylcynichrodenecarboxamide (18)*

Cynichrodenoyl chloride was prepared as a red-brown residue from 1.00 g of cynichrodenoic acid as described above. Diethyl ether (20 ml) and 3.87 g (41.6 mmol) of aniline were added and the mixture was stirred for 30 min. Following removal of the solvent, the residue was taken up in 50 ml of methylene chloride and washed with water. After drying over magnesium sulfate, the solution was concentrated to a dark brown residue which was chromatographed on a dry-packed column (4 × 9 cm) of silica gel. Elution of the column with benzene/ether gave an orange band which upon removal of the solvent under vacuum gave *N*-phenylcynichrodenecarboxamide, 0.99 g (76%). An analytical sample, m.p. 153 °C, was obtained by vacuum sublimation at 140 °C/0.1 Torr. (Found: C, 52.05; H, 3.28; N, 8.55. $C_{14}H_{10}CrN_2O_4$ calc.: C, 51.18; H, 3.13; N, 8.69%). ^{1}H NMR δ 5.12 (2H, t, $H_{3,4}$); 5.72 (2H, t, $H_{2,5}$); 7.15–7.50 (6H, m, NH and C_6H_5). IR ($CDCl_3$) 3450 (m), 2040 (vs), 1968 (vs), 1710 (vs), 1600 (m), 1528 (s), 1500 (m), 1468 (w), 1440 (s), 1418 (w), 1380 (w), 1320 (m), 1270 (w), 1240 (w), 1140 (w), 1030 (w), 828 (w), 630 (m) cm^{-1}. MS *m/e* 322 (M^+).

N,N-*Dimethylcynichrodenecarboxamide (17)*

Cynichrodenoyl chloride was prepared as a red-brown solid from 1.00 g of cynichrodenoic acid as described above. Diethyl ether (20 ml) was added and dry dimethylamine was passed through the solution for 30 min. After removal of the solvent, the residue was taken up in 50 ml of methylene chloride and the solution washed with water, dilute hydrochloric acid, and again with water. After drying over magnesium sulfate, the solution was concentrated to a dark brown residue which was chromatographed on a dry-packed column (4 × 9 cm) of silica gel. Elution of the column with benzene/ether gave an orange band which upon removal of the solvent under vacuum gave *N,N*-dimethylcynichrodenecarboxamide, 0.91 g (82%). An analytical sample, m.p. 58 °C, was obtained by vacuum sublimation at 45 °C/0.1 Torr. (Found: C, 43.78; H, 3.79; N, 10.38. $C_{10}H_{10}CrN_2O_4$ calc.: C, 43.80; H, 3.68;

N, 10.22%). ^{1}H NMR ($CDCl_3$) δ 3.12 (6H, s, CH_3); 5.09 (2H, t, $H_{3,4}$); 5.60 (2H, t, $H_{2,5}$). IR (CH_2Cl_2) 2950 (m), 2030 (vs), 1960 (vs), 1710 (vs), 1628 (vs), 1502 (s), 1460 (w), 1398 (s), 1370 (w), 1232 (w), 1108 (s), 1060 (m), 1040 (w), 940 (w), 860 (m), 830 (s), 665 (m), 638 (s), 628 (s) cm^{-1}. MS *m/e* 246 $(M - CO)^+$.

Benzyl cynichrodenoate (20)

Cynichrodenoyl chloride was prepared as a red-brown solid from 1.00 g of cynichrodenoic acid as described above. Diethyl ether (20 ml), 20 drops of pyridine and 4.32 g (4.20 ml, 40.2 mmol) of benzyl alcohol were added and the mixture was stirred for 1 h. After removal of the solvent, the residue was taken up in 50 ml of methylene chloride and the solution was washed with water several times. After drying over magnesium sulfate, the solution was concentrated to a dark red residue which was chromatographed on a dry-packed column (4 × 9 cm) of silica gel. Elution of the column with benzene gave a red band which upon removal of the solvent under vacuum gave the benzyl ester, 1.12 g (82%). An analytical sample was obtained by molecular distillation at 130 °C/0.1 Torr as a red liquid. (Found: C, 53.41; H, 3.46; N, 4.11. $C_{15}H_{11}CrNO_5$ calc.: 53.42; H, 3.29; N, 4.15%). ^{1}H NMR ($CDCl_3$) δ 5.08 (2H, t, $H_{3,4}$); 5.22 (2H, s, CH_2); 5.78 (2H, t, $H_{2,5}$); 7.36 (5H, s, C_6H_5). IR ($CDCl_3$) 2018 (vs), 1970 (vs), 1720 (vs), 1470 (m), 1380 (m), 1285 (s), 1210 (w), 1142 (s), 1060 (w), 1040 (m), 950 (m), 832 (m), 668 (w), 625 (m) cm^{-1}. MS *m/e* 337 (M^+).

Ferrocenylmethyl cynichrodenate (21)

Cynichrodenoyl chloride was prepared as a red-brown solid from 1.00 g of cynichrodenoic acid as described above. To a solution of the acid chloride in 20 ml of diethyl ether was slowly added a previously prepared solution ferrocenylmethanol [13] (3.00 g, 13.9 mmol) in 2 ml of pyridine, and the reaction mixture was stirred for 1 h. Diethyl ether (50 ml) was added and the solution was washed with water several times, once with dilute hydrochloric acid, and once again with water. After drying over magnesium sulfate, the solution was concentrated and chromatographed on a dry-packed column (4 × 9 cm) of silica gel. Elution of the column with hexane/benzene gave a yellow band which upon removal of the solvent under vacuum gave the ferrocenylmethyl ester, 0.83 g (46%). An analytical sample was obtained by vacuum sublimation at 100 °C/0.1 Torr as orange-yellow crystals, m.p. 114 °C. (Found: C, 51.55; H, 3.57; N, 3.05. $C_{19}H_{15}CrFeNO_5$ calc.: C, 51.26; H, 3.40; N, 3.15%). ^{1}H NMR ($CDCl_3$) δ 4.18 (5H, s, FeC_5H_5); 4.26 (4H, t, FeC_5H_4); 5.02 (2H, s, CH_2); 5.06 (2H, t, $CrCpH_{3,4}$); 5.74 (2H, t, $CrCpH_{2,5}$). IR ($CDCl_3$) 3120 (w), 2040 (vs), 1970 (vs), 1550 (w), 1475 (m), 1420 (w), 1380 (m), 1285 (s), 1240 (w), 1145 (s), 1095 (w), 1060 (w), 1040 (m), 1002 (w), 830 (m), 630 (m) cm^{-1}. MS *m/e* 445 (M^+).

Cynichrodenecarboxylic anhydride (22)

Cynichrodenoyl chloride was prepared as a red-brown residue from 1.00 g of cynichrodenoic acid as described above. Five milliliters of THF and 5 ml of pyridine were added and the mixture stirred for 15 min. After heating the reaction mixture in an oil bath at 60 °C for 5 min, 4 g of ice and then 2 ml of concentrated hydrochloric acid were added slowly. The solution was extracted with 100 ml of diethyl ether and the extracts washed several times with water, once with sodium bicarbonate solution, and once again with water. After drying over magnesium

sulfate, the solution was concentrated and the residue was chromatographed on a dry-packed column (4 × 9 cm) of Florisil. Elution of the column with benzene/ether gave a red band which upon removal of the solvent under vacuum gave cynichrodenecarboxylic anhydride, 0.20 g (30%). An analytical sample was obtained by vacuum sublimation at 120 °C/0.1 Torr as orange crystals, m.p. 164 °C. (Found: C, 40.70; H, 1.98; N, 6.16. $C_{18}H_8Cr_2N_2O_9$ calc.: 40.35; H, 1.69; N, 5.88%). ^{1}H NMR (acetone-d_6) δ5.38 (2H, t, $H_{3,4}$); 5.88 (2H, t, $H_{2,5}$). IR ($CDCl_3$) 2040 (s), 1970 (s), 1715 (s), 1370 (w), 1260 (m), 1070 (m), 1054 (m), 1040 (m), 1010 (m), 900 (w), 880 (w), 830 (w), 700 (w), 628 (w) cm^{-1}.

Reaction of acetylcynichrodene (2) with phenyllithium

A solution of phenyllithium (2.02 mmol) was added to a solution of acetylcynichrodene (0.500 g, 2.03 mmol) in 100 ml of diethyl ether. The reaction mixture was stirred at room temperature for 2 h. Then 100 ml of ice was added slowly followed by 5 drops of concentrated hydrochloric acid. The aqueous and organic layers were separated. The organic layer was washed with water several times and dried with anhydrous magnesium sulfate. The solution was filtered and the solvent was removed under vacuum to give a residue which was chromatographed on a dry-packed column (4 × 9 cm) of alumina. Elution of the column with benzene gave a yellow band which upon removal of the solvent gave 0.064 g (13%) of 1,3-dicynichrodenylbut-2-en-1-one (**24**), followed by another band which upon removal of the solvent gave 0.38 g (60%) of 1-cynichrodenyl-1-phenylethanol (**23**) [5].

An analytical sample of **24** was obtained by molecular distillation at 140 °C/0.1 Torr. (Found: C, 45.87; H, 2.98; N, 5.64. $C_{18}H_{12}Cr_2N_2O_7$ calc.: C, 45.78; H, 2.56; N, 5.93%). ^{1}H NMR ($CDCl_3$) δ 2.35 (3H, d, CH_3); 5.18 (4H, m, $H_{3,4}$); 5.52 (2H, t, $H_{2,5}$); 5.78 (2H, t, $H_{2,5}$); 6.50 (1H, q, =CH). IR ($CDCl_3$) 3110 (w), 2030 (vs), 1960 (vs), 1700 (vs), 1650 (s), 1460 (m), 1380 (m), 1290 (m), 1080 (m), 1040 (m), 960 (w), 820 (s), 660 (w), 620 (s) cm^{-1}.

Reaction of acetylcynichrodene (2) with methyllithium

A solution of methyllithium (2.02 mmol) was added to a solution of acetylcynichrodene (0.500 g, 2.03 mmol) in 100 ml of diethyl ether. The reaction mixture was stirred at room temperature for 2 h. Then 100 ml of ice was slowly added followed by 5-drops of concentrated hydrochloric acid. The aqueous and organic layers were separated. The organic layer was washed with water several times and dried with anhydrous magnesium sulfate. The solution was filtered and the solvent removed under vacuum to give a residue which was chromatographed on a dry-packed column (4 × 9 cm) of silica gel. Elution of the column with benzene gave an orange band which upon removal of the solvent gave 1-hydroxy-1-methylethylcynichrodene, 0.49 g (93%). The product was characterized by spectral comparisons with a known sample [5].

Reaction of acetylcynichrodene (2) with n-butyllithium

A solution of n-butyllithium (4.05 mmol) was added to a solution of acetylcynichrodene (1.00 g, 4.05 mmol) in 100 ml of diethyl ether. The reaction mixture was stirred at room temperature for 4 h. Ice (100 ml) was added slowly

followed by 5 drops of concentrated hydrochloric acid. The aqueous and organic layers were separated. The organic layer was washed with water several times and dried with anhydrous magnesium sulfate. The solution was filtered and the solvent was removed under vacuum to give a residue which was chromatographed on a dry-packed column (4 × 9 cm) of alumina. Elution of the column with benzene gave a yellow band which upon removal of the solvent produced a 1 : 1 mixture of 0.32 g (33%) of 1,3-dicynichrodenylbut-2-en-1-one (**24**) and 0.40 g (33%) of 2-cynichrodenylhexan-2-ol (**25**), as evidenced by ^{1}H NMR spectrometry.

Reaction of acetylcynichrodene (2) with potassium t-butoxide

Potassium t-butoxide (2.02 mmol) was added to a solution of acetylcynichrodene (0.500 g, 2.03 mmol) in 100 ml of isopropanol/ether. The reaction mixture was refluxed for 12 h. After hydrolysis and purification, a 50% yield of acetylcynichrodene was recovered.

Reaction of acetylcynichrodene (2) with lithium diisopropylamide

To a solution of phenyllithium (2.03 mmol) in 50 ml of diethyl ether was added dropwise diisopropylamine (0.211 g, 2.03 mmol). The reaction mixture was stirred at room temperature for 4 h. Acetylcynichrodene (0.500 g, 2.03 mmol) was added and stirring was continued for 4 h. Then 100 ml of ice was added slowly, followed by 5 drops of concentrated hydrochloric acid. The aqueous and organic layers were separated, the organic layer was washed with water several times and dried with anhydrous magnesium sulfate. The solution was filtered and the solvent was removed under vacuum to give a residue which was chromatographed on alumina. Elution of the column with benzene gave a yellow-orange band which upon removal of the solvent gave 0.26 g (54%) of 1,3-dicynichrodenylbut-2-en-1-one (**24**), whose spectral properties were identical to those of **24** described above.

Cinnamoylcynichrodene (27)

To a solution of phenyllithium (2.03 mmol) in 50 ml of diethyl ether was added diisopropylamine (0.210 g, 2.03 mmol). The reaction mixture was stirred at room temperature for 4 h. Acetylcynichrodene (0.500 g, 2.03 mmol) and benzaldehyde (0.200 g, 2.03 mmol) were added and the mixture was stirred for 3 h. Ice (100 ml) was added slowly, followed by 5 drops of concentrated hydrochloric acid. The aqueous and organic layers were separated. The organic layer was washed with water several times and dried with anhydrous magnesium sulfate. The solution was filtered and the solvent removed under vacuum to give a residue which was chromatographed on a dry-packed column (4 × 9 cm) of silica gel. Elution of the column with benzene gave a red band which upon removal of the solvent gave cinnamoylcynichrodene, 0.60 g (89%). An analytical sample, m.p. 94 °C, was obtained as orange crystals by vacuum sublimation at 80 °C/0.1 Torr. (Found: C, 57.80; H, 3.59; N, 4.17. $C_{16}H_{11}CrNO_4$ calc.: C, 57.67; H, 3.33; N, 4.20%). ^{1}H NMR δ 5.25 (2H, t, $H_{3,4}$); 5.87 (2H, t, $H_{2,5}$); 6.96 (1H, d, =CH-Ph); 7.60 (5H, m, C_6H_5); 7.75 (1H, d, CO-CH=). IR ($CDCl_3$) 2010 (vs), 1960 (vs), 1700 (vs), 1655 (s), 1600 (s), 1575 (m), 1450 (m), 1375 (m), 1330 (m), 1300 (w), 1285 (w), 1240 (w), 1074 (m), 1040 (w), 975 (w), 830 (w), 630 (m) cm^{-1}. MS *m/e* 335 (M^+).

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References and notes

1 The trivial name cynichrodene has been proposed by analogy to the shortened names cymantrene and benchrotrene for (η^5-cyclopentadienyl)tricarbonylmanganese and (η^6-benzene)tricarbonylchromium, respectively (see appropriate footnotes in references 4 and 5).
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